

A Guide to Practical Radio/ chemistry

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Vol.2

«Руководство
к практическим
занятиям
по
радиохимии»

Под редакцией
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A Guide to Practical Radiochemistry

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Part III Chemical Properties, Methods of Preparation, and Analysis of Radioactive Elements

Chapter 10 The Chemistry and Analysis of Technetium [1]

Experiment 10.1. SEPARATION OF ^{99}Tc , ITS IDENTIFICATION, AND THE PREPARATION OF PURE COMPOUNDS [2-6]

Technetium Tc is an artificial radioactive element; it has many isotopes with mass numbers from 92 to 107 and half-lives from several seconds to 2×10^6 years. As regards its chemical properties, it is an analogue of rhenium and manganese. The chemical properties of technetium in tracer amounts are studied for the isotopes ^{95}Tc , ^{96}Tc , ^{97m}Tc , and ^{99m}Tc , and in weight amounts for the long-lived isotope ^{99}Tc with a half-life of 2.12×10^5 years.

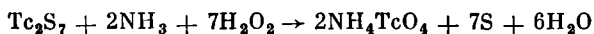
Technetium-99 is a daughter element of ^{99}Mo , and it is prepared from the fission products of uranium or from molybdenum irradiated by neutrons: $^{98}\text{Mo}(n, \gamma)^{99}\text{Tc}$. Spectrally pure metallic molybdenum or its oxide MoO_3 are used as the target. The neutron capture cross section for this reaction is 0.13 barn.

Upon irradiation with high-density fluxes of neutrons, relatively large amounts of ^{99}Tc can be obtained. For example, when 100 g of MoO_3 are irradiated during two months with a flux of 10^{14} neutron/($\text{cm}^2 \cdot \text{s}$), from 1 to 1.5 mg of ^{99}Tc accumulate in the sample*.

Technetium is recovered from any kind of raw material in its highest oxidation state VII, which is the most stable one. An effective way of recovering it is extraction with the use of acetone as the extracting agent. In this case, it is possible to increase the technetium concentrate purification coefficient to 10^4 and thus recover radiochemically pure technetium. The purity of the isotope is monitored according to the maximum energy of its β -radiation (0.3 MeV) by the method of complete absorption in aluminium or by the method of β, γ -spectroscopy.

The scheme of technetium purification includes its transfer into sparingly soluble compounds such as its heptasulphide Tc_2S_7 , tetraphenyl arsonium pertechnetate $(\text{C}_6\text{H}_5)_4\text{As} \times \text{AsTcO}_4$, and the dioxide TcO_2 .

Technetium heptasulphide Tc_2S_7 is a dark brown substance. It is prepared by acting with H_2S on acid solutions of pertechnetates. In a hydrochloric acid medium, a precipitate may appear at an HCl concentration of not over 5 M; Tc_2S_7 is precipitated quantitatively from a 1-3 M solution of HCl , while it is already impossible to precipitate Tc_2S_7 from a 9 M solution of HCl . Technetium heptasulphide coprecipitates with FeS , PbS , CuS , MnS , Re_2S_7 , PtS_2 , PtS , and ZnS . Technetium heptasulphide readily reacts with hydrogen peroxide in an alkaline medium:



At 1100 °C, Tc_2S_7 is reduced by hydrogen to metallic Tc. When heated to 100 °C, Tc_2S_7 is completely carried off by a stream of chlorine.

Technetium dioxide TcO_2 differs from the oxides of its analogues (ReO_2 and MnO_2) in that at an elevated temperature (900-1000 °C) it sublimes without decomposition. After three hours of heating in a vacuum at 300 °C, the hydroxide $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ becomes completely dehydrated, at 900 °C it

* Molybdenum irradiated with slow neutrons is held for a prolonged period in storage up to complete decay of the ^{99}Mo , and also of the accompanying radiochemical impurities.

begins to sublime, and at 1000 °C it sublimates rapidly. Technetium dioxide TcO_2 is prepared electrolytically by the reduction of pertechnetates, and also by the hydrolysis of the ion TcCl_6^{2-} . In alkaline solutions, technetium dioxide is readily oxidized by hydrogen peroxide and even by the oxygen of the air with the formation of the ion TcO_4^- .

Technetium dioxide dissolves with difficulty in 6 *N* HCl with the formation of the ion TcCl_6^{2-} .

Ammonium pertechnetate NH_4TcO_4 is a white salt isomorphous to NH_4ReO_4 . Ammonium pertechnetate is prepared upon the neutralization of pertechnetic acid with NH_4OH or upon the dissolving of TcO_2 in an aqueous solution of $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$. Ammonium pertechnetate is stable in air at a temperature of 100 °C. Hydrogen reduces NH_4TcO_4 to the metal at a temperature of 500-600 °C.

Tetraphenyl arsonium pertechnetate $(\text{C}_6\text{H}_5)_4\text{AsTcO}_4$ is a compound poorly soluble in water, but well in chloroform. It forms white needle-shaped crystals. It is prepared in precipitating ions of TcO_4^- by adding a solution of tetraphenyl arsonium chloride.

Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window counter. An apparatus for reducing technetium salts with hydrogen. A centrifuge. A drying cupboard. A microbalance. A flask for 100 ml with a reflux condenser transforming into a direct cooler. A Kipp gas generator (small size). A water bath. Separatory funnels for 100, 20, and 10 ml. A micropipette for 0.1 ml. Filtering funnels. Syringes. Beakers. Measuring cylinders. Test tubes.

Radioactive Substances. Molybdenum irradiated with neutrons or a technetium concentrate.

Reagents. Acetone. Tetraphenyl arsonium chloride. Solutions: 1 *N* NH_4OH ; 5 *N* NaOH ; concentrated HNO_3 ; 3 *N* HCl ; 30% H_2O_2 (all the reagents must be of the especially pure grade).

Performance of Work

(a) Preparation of Technetium Concentrate

Oxidize spectrally pure MoO_3 (1 g) irradiated in a nuclear reactor by an integral flux of 5×10^{21} neutron/cm² kept for two years with concentrated HNO_3 for transferring the molybdenum into the hexavalent, and the technetium into the heptavalent states. Perform the operation in the flask with the reflux condenser placed in a glove box. Add nitric

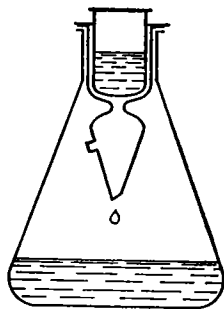


Fig. 10.1 A way of heating a microbeaker in water vapour

acid in portions until a precipitate is obtained. Next distil off the surplus nitric acid in the same apparatus, but after replacing the reflux condenser with a direct cooler. Repeat the distillation a number of times by adding water to the reaction flask up to complete elimination of the acid residues. Transfer the residue remaining after evaporation of the product with a spatula into a porcelain beaker and dissolve it in water with the addition of a few drops of 30% H_2O_2 and a solid alkali so that the concentration of the free alkali in the solution will be 5 N .

Extract the technetium from the sodium molybdate solution in the separatory funnel with a half volume (with respect to the aqueous phase) of acetone with vigorous agitation during 10 min. After settling, separate the acetone layer and wash it twice with a 5 N solution of NaOH (1/5 of the volume of the acetone).

After separating the layers, transfer the organic phase to the flask with the direct cooler and distil off the acetone. Neutralize the residue in the flask with hydrochloric acid and establish an acidity of the solution of 1-2 N with respect to HCl . Work with the microgramme amounts of technetium obtained may be performed without any special protection in accordance with the safety rules for work of class III.

(b) Technetium Heptasulphide

Precipitate Tc_2S_7 from a 1-2 N solution of the technetium concentrate with respect to HCl containing 100 μg of ^{99}Tc . To do this, pass hydrogen sulphide through the solution

heated on a water bath (Fig. 101.). Centrifuge the black-brown precipitate and wash it several times with water acidified with hydrochloric acid, removing the washing water with a pipette. Transfer the heptasulphide precipitate with a pipette into a glass bowl 20 mm in diameter and dry it in the drying cupboard at 110 °C.

Determine the maximum energy of the β -radiation of the isotope according to its absorption in aluminium or in a β -spectrometer. Compare the result obtained with published data.

(c) Tetraphenyl Arsonium Pertechnetate

Dissolve the Tc_2S_7 precipitate obtained in the preceding experiment (b) (in the same bowl) in a 1 *N* solution of NH_4OH with the addition of hydrogen peroxide (a few drops). Perform this operation carefully to prevent losses of technetium. Add the ammonia and hydrogen peroxide solutions dropwise with a pipette. Transfer all the contents from the bowl into a centrifuge tube with another pipette and heat on a water bath (carefully!). Separate the sulphur formed as a result of the reaction in a centrifuge. Dilute the transparent solution of the formed ammonium pertechnetate with an admixture of compounds of non-radioactive elements (Mo, Fe, etc.) with water and bring the volume up to 5 ml. Take three parallel samples each containing 0.005 ml with the micropipette (Fig. 10.2) and apply them onto a Terylene film (3 μm thick). Determine the absolute activity A_1 of a sample according to a standard.

Next heat the solution on a water bath (see Fig. 10.1), add tartaric acid and sodium chloride in an amount such that their concentration will be 0.6 and 0.5 *M*, respectively. Keep the pH of the solution at about 8. Add a surplus amount of a 1% solution of tetraphenyl arsonium chloride while stirring with a rod. The final volume must not exceed 10 ml. After white acicular crystals precipitate, cool the contents of the test tube with icy water and let it stand for several hours. Next separate the precipitate in a centrifuge, wash it several times with icy water, transfer it with a pipette into a weighed quartz boat and dry at 110 °C. Collect the centrifugate in a graduated cylinder, and take three parallel samples each containing 0.005 ml with a micropipette from the cylinder and also apply them onto a Terylene film. Determine the total activity A_2 of the solution.

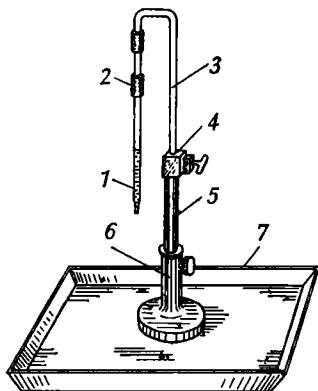


Fig. 10.2.

Sampler:

1—micropipette; 2—rubber connecting tube; 3—glass tube;
4—chamber with glycerin; 5—helical piston; 6—support;
7—pan

According to the difference between the quantities A_1 (the activity before precipitation of the salt) and A_2 (the activity after precipitation of the salt) establish the completeness of precipitation of the compound $(C_6H_5)_4AsTcO_4$ (in %), adopting A_1 as 100%. Proceeding from the values of the quantity $A_1 - A_2$ and the specific activity of technetium equal to 629 GBq/kg (17 μ Ci), determine the mass of the recovered salt $(C_6H_5)_4AsTcO_4$. Control the value obtained by weighing the precipitate on the microbalance.

*(d) Technetium Dioxide
and Ammonium Pertechnetate*

Technetium dioxide is prepared by reducing tetraphenyl arsonium pertechnetate with hydrogen. Place the salt in a thin layer in a quartz boat and put the latter into a tubular microfurnace (Fig. 10.3). Pass hydrogen through the entire system during one hour without switching on the furnace for heating until the air is completely removed. After convincing yourself that the emerging hydrogen is pure, slowly raise the temperature of the furnace up to 260 °C, controlling the heating with the aid of a rheostat. Pass hydrogen through the system at a rate of 30-50 ml/min, also during one hour. Extract the preparation from the furnace only after complete cooling of the entire arrangement.

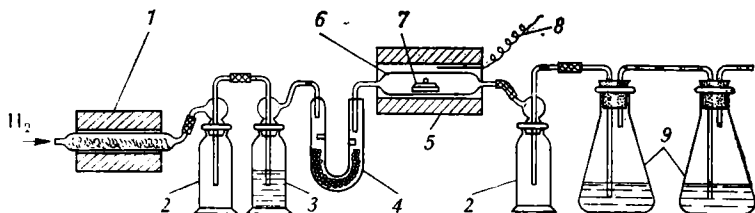


Fig. 10.3. Arrangement for preparing TcO_2 :

1—furnace with quartz tube filled with copper shavings; 2—protective bottles; 3—wash bottle with concentrated H_2SO_4 ; 4—tube with P_2O_5 ; 5—furnace; 6—quartz tube; 7—quartz boat with lid for weighed sample of substance being studied; 8—thermocouple; 9—absorbing bottles with 0.1 N NaOH

Prepare the hydrogen in a Kipp gas generator by acting with sulphuric acid of an especially pure grade with a density of 1.84 g/cm^3 (1 volume of concentrated H_2SO_4 and 8 volumes of water) on especially pure granulated zinc. Place a trap with driers in the path of the stream of hydrogen to the furnace, and a water seal at the end of the system.

The black powder obtained is technetium dioxide.

Technetium dioxide is used to prepare NH_4TcO_4 . For this purpose, oxidize it with hydrogen peroxide in an NH_4OH medium as described in Sec. (c) of the present experiment. After evaporation of the surplus NH_4OH and hydrogen peroxide, white crystalline ammonium pertechnetate precipitates. Dissolve the precipitate in 1 ml of water.

Determine the concentration of technetium in the solution obtained by the radiometric method after measuring the absolute activity of the sample [see Sec. (c) of the present experiment].

Experiment 10.2. METHODS OF QUANTITATIVE ANALYSIS OF TECHNETIUM COMPOUNDS [1-6]

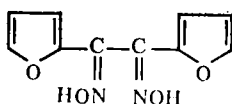
The determination of the absolute activity according to the radiation of the isotope ^{99}Tc in a 4π counter should be included among the methods of quantitative analysis of technetium. It must be remembered that complications are introduced into this method by the low energy of the β radiation of the isotope ^{99}Tc (0.3 MeV). The measurement of its absolute activity is hindered by insignificant admixtures of various salts and even dust.

Polarography yields very accurate results in the quantitative determination of technetium when its content in a solution is up to 10^{-3} g. The method is suitable, however, only for an absolutely pure preparation of technetium. For analytical purposes, the $\text{Tc}^{\text{VII}} \rightarrow \text{Tc}^{\text{IV}}$ half-wave of reduction is used in neutral solutions at a potential of -0.8 V.

A sufficiently widespread method of analysis is the spectrophotometric one according to the density of light absorption by the ion TcO_4^- in HClO_4 , HCl , H_2O , and also by the ion TcCl_6^{2-} in HCl .

Emission spectral analysis gives satisfactory results. Here it is convenient to use Meggers's tables that contain data for over 2000 lines of neutral and ionized technetium atoms in the region of 226 to 883 nm.

Colorimetric methods of analysis are in great favour. Coloured technetium compounds are used for this purpose, namely, with α -glycolic acid, thiourea, dimethylglyoxime, methyl violet, α -benzyldioxime, *o*-cyclohexanedione-1,2-dioxime, as well as thiocyanogen complexes." A valuable reagent for the colorimetric determination of technetium is α -furyldioxime:



The presence of a tenfold (10^{-4} M) amount of molybdenum with respect to technetium (10^{-5} M) does not virtually change the value of the optical density of a complex compound. The sensitivity of the indicated reactions fluctuates from 0.7 to 0.1 $\mu\text{g/ml}$.

Analytical methods have been developed for determining technetium in a solution that combine the selective extraction of its compound with acetone and the following spectrophotometry (the error in determining does not exceed about 5%), and also with the use of β -spectroscopy (the accuracy of the method in this case is about 2%). The automatic micropipette "Eppendorf Pipette" is recommended for taking samples.

The weight method of analysis customarily used in determining rhenium, i.e. determination in the form of nitron,

tetraphenyl arsonium or tetraphenyl phosphonium pertechnetates is not quantitative and for this reason has found no use.

Equipment and Reagents

Equipment and Utensils. A spectrophotometer SF-4 with 2 quartz planchets (layer thickness 1 cm). A counting installation with a 4π counter and a Terylene film having a thickness of not over 3×10^{-6} M. A micropipette for 0.1 and 0.2 ml. Measuring cylinders for 10 ml (2).

Radioactive Substances. A 10^{-3} - 10^{-6} M solution of NH_4TcO_4 .

Reagents. Solutions: 0.1 N HCl (grade "especially pure"); 0.01 M α -furyldioxime in acetone; 10% SnCl_2 .

Performance of Work

Prepare 3 ml of an aqueous solution of ammonium pertechnetate with a concentration of about 10^{-4} M in a 10-ml measuring cylinder, using bidistilled water. Determine the amount of technetium by the radiometric method (see Experiment 10.1c).

Transfer the solution into the quartz planchet of the spectrophotometer and measure its optical density at λ from 220 to 350 nm. Plot the optical density D versus the wavelength λ .

Repeat the experiment with a solution of NH_4TcO_4 in 0.1 N HCl.

Determine the molar extinction coefficient of the ion TcO_4^- in a pure aqueous solution and a 0.1 N solution of HCl at the largest value of the optical density of the solution.

Add 1 ml of 1 N hydrochloric acid, 2.5 ml of an 0.01 M solution of α -furyldioxime in acetone, and 0.5 ml of a 10% solution of SnCl_2 to 0.3 ml of a solution of NH_4TcO_4 with a concentration of 200 $\mu\text{g/ml}$. Determine the final concentration of the technetium by the radiometric method and according to the adsorption spectrum at $\lambda = 300$ -1200 nm.

Calculate the molar extinction coefficient of the coloured complex compound of technetium with α -furyldioxime at the highest value of the optical density of the solution.

Experiment 10.3. BEHAVIOUR OF IONS TcO_4^- AND TcCl_6^{2-} IN AQUEOUS SOLUTIONS [2, 4, 6]

It is general knowledge that Tc^{VII} is in the form of the ion TcO_4^- in aqueous solutions within a broad range of the pH*. This ion is stable like ReO_4^- and unlike MnO_4^- .

It has been indicated in the literature that Tc^{VII} can be reduced by hydrazine, hydroxylamine, and ascorbic and hydrochloric acids. For example, already 4 *N* hydrochloric acid reduces the ion TcO_4^- to TcCl_6^{2-} upon prolonged heating of the solution on a water bath.

Tetravalent technetium in the form of the hexachlorotechnetate ion TcCl_6^{2-} can be prepared by dissolving technetium dioxide in 6 *M* hydrochloric acid by heating for three hours at 90 °C. The ion TcCl_6^{2-} is stable only in 1 *M* (not lower) hydrochloric acid solutions. In a neutral medium as a result of hydrolysis, the hydrated dioxide is formed, which is gradually oxidized by the oxygen of the air. In an alkaline and sulphuric acid media, Tc^{IV} is immediately oxidized by the oxygen of the air to Tc^{VII} , and the absorbed spectrum of the solution in this case corresponds to the spectrum of the ion TcO_4^- .

Equipment and Reagents

Equipment and Utensils. A spectrophotometer SF-4 with quartz planchets (thickness of layer 1 cm). A water bath. Measuring cylinders for 10 ml. Micropipettes for 0.1-0.2 ml.

Radioactive Substances. A solution of NH_4TcO_4 (10^{-5} *M*). 20 µg of TcO_2 .

Reagents. Solutions: concentrated HCl "especially pure", 0.1 *N* NaOH "especially pure".

Performance of Work

Prepare 4 ml of a 10^{-5} *M* aqueous solution of ammonium pertechnetate (see Experiment 10.1). Determine the technetium content according to the absorption spectrum of the prepared solution at $\lambda = 220\text{-}350$ nm. After this, transfer the solution into a 10-ml measuring cylinder with a ground-glass stopper. Bring the concentration of the solution up to 6 *N* with respect to HCl and heat it on a water bath during

* The ion TcO_4^- in water greatly absorbs light in the ultraviolet region of the spectrum.

six hours. After every two hours, register the absorption spectrum of the cooled solution.

Dissolve TcO_2 in 4 ml of 6 *N* hydrochloric acid with heating during three hours on a water bath. Transfer the solution to the planchet of the spectrophotometer and register its absorption spectrum at $\lambda = 220\text{--}350$ nm.

Establish a neutral reaction in the solution (by adding NaOH or KOH) and register its absorption spectrum.

Next bring the pH of the solution up to 8-9 and again register the absorption spectrum.

Draw graphs of how the change in the optical density *D* depends on the wavelength λ . Using published data, arrive at a conclusion on the oxidation state of technetium in the studied solutions.

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Chapter 11 The Chemistry and Analysis of Uranium [1-5]

Experiment 11.1. METHODS OF BREAKING DOWN URANIUM ORES [5]

A. ACID METHOD

The method of breaking down uranium raw material with the use of acids is the most widespread one at present. The acid method is used to decompose poorly soluble uranium

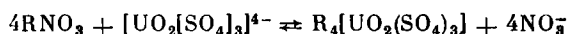
ores containing oxides of Ti, Th, Nb, Ta, and the rare-earth metals that are not decomposed by alkaline reagents. When ores contain compounds of tetravalent uranium, the acid treatment is performed by adding oxidizing agents (nitric acid, pyrolusite, sodium chlorate and the like) to the mixture. The uranium passes into the solution in the form of uranyl salts.

The uranium ore is often roasted in the air before the acid treatment to remove the organic impurities, oxidize the sulphides, and decompose the carbonates. Sometimes various salts are added to the mixture to be treated thermally. Here the uranium oxides transform into uranates well soluble in acids and carbonate solutions, while the impurities transform into poorly soluble compounds. For example, uranium ores containing silver and gold are roasted in the presence of sodium chloride, which makes it possible to distil off the gold chloride and transfer the silver into its chloride that does not pass into the solution when treated with acids. Roasting with sodium chloride is also used when breaking down uranium-vanadium minerals.

Uranium ores are most often broken down in the industry with sulphuric acid as the cheapest reagent that also ensures a high degree of purification (90-99%). The treatment with the acid is performed in the cold or at 40-50 °C.

Depending on the composition of the ores being processed, some accompanying impurities (salts of Fe and Al, Cu, Ni, Mn, etc.) pass into the solution together with the uranyl salts. The uranium is recovered from the acid solutions by chemical precipitation, ion exchange, or by extraction with organic solvents.

Ion exchange separation is based on the adsorption of the anion uranium sulphate complexes by strongly basic anion exchange resins and the following desorption by washing out the uranyl ions bound in the anion complex with acidified solutions of salts. The exchange process can be written as follows:



The solvents used to extract the uranyl salts include diethyl ether, tributyl phosphate (TBP), tenoyltrifluoroacetone (TTA), methylisobutylketone (hexone), methylethylketone, dodecylphosphoric acid (DDPA), and ethylhexylphosphoric acid (EHPA). The esters of phosphoric acid and alkyl

amines are the most effective solvents of uranium compounds and, therefore, extracting agents from sulphuric acid solutions. TBP has found no use, however, because it does not have sufficient selectivity in this case (see Vol. 1, Chap. 1).

Equipment and Reagents

Equipment and Utensils. A crucible furnace (for 800 °C). A separatory funnel for 500 ml. A burette. A porcelain crucible. A porcelain beaker for 500 ml.

Radioactive Substances. Uranium ore.

Reagents. Anion exchanger AV-17. TBP. Solutions: 1 *M* and 2 *M* H₂SO₄; 1 *M* HCl; 10 *M* HCl; 12 *M*, 0.1 *N* HNO₃; saturated BaCl₂; 1 *M* NH₄NO₃; 1 *M* Na₂CO₃; 0.1 *M* DDPA (or EHPA) in kerosene.

Performance of Work

Place a weighed sample of the uranium ore (200 g) into the porcelain crucible and heat it in the crucible furnace at 500-600 °C, simultaneously passing air or oxygen into the furnace. Do this work *under a hood*! Continue the heating for 30 min. Next extract the crucible from the furnace, cool it to room temperature, and triturate the substance in an agate mortar (*put on a respirator!*). Again put the substance in the crucible into the furnace and roast it in the same conditions for another hour. After cooling the ore, transfer it into the 500-ml porcelain beaker. Add 100 ml of a mixture of 2 *M* sulphuric acid (95 ml) and 12 *M* nitric acid (5 ml) to the dry substance with stirring. Place the beaker with the pulp on the water bath and heat for five hours. More prolonged treatment with the acid also ensures more complete decomposition of the ore.

Add 50 ml of hot water and 5 ml of a saturated solution of barium chloride to the mixture, and separate the solution from the solid residue by filtration through a fluted filter. Wash the substance remaining on the filter with small portions of hot water until the washing water becomes absolutely colourless. Combine the solution and the washing water.

Separate the uranium compounds from the solution by the methods of extraction with organic solvents or ion exchange.

(a) Extraction of Uranyl Salts with Organic Solvents

Compounds of Fe^{III} are readily extracted by alkyl phosphates, therefore it is first necessary to transfer Fe^{III} into Fe^{II} whose compounds are difficult to extract. For this purpose, add 2-3 g of iron shavings to the sulphuric acid solution obtained (or pass hydrogen sulphide through the solution for 30 min). Here partial reduction of the uranyl salts will occur, which is not dangerous, however, because solutions of DDPA and EHPA are also good extracting agents of compounds of U^{IV} . Shake the solution in the separatory funnel with a 0.1 *M* solution of DDPA in kerosene (the ratio of the aqueous and organic phases is 7 : 1). After separation of the phases, separate the aqueous phase from the organic one. Repeat the extraction at least three times. Combine the organic phases, and then perform reextraction with a 10 *M* solution of HCl (the ratio of the organic and aqueous phases is 7 : 1). Repeat this operation at least three times. Combine the hydrochloric acid extracts and evaporate them on the water bath until the initial volume diminishes by about one-third. Add NH_4OH to the solution to precipitate ammonium diuranate from it. Produce uranous-uranic oxide by roasting the ammonium diuranate at 100 °C. Weigh the preparation.

When using a 0.1 *M* solution of EHPA in kerosene as the extractant, add TBP (up to 0.1 *M*) to the solution to prevent the formation of a third liquid phase (at the expense of sodium and ammonium salts). It is convenient to wash out the uranium compounds in this case with a 1 *M* solution of soda after the vanadium compounds have been removed from the extract by treatment with 1 *M* H_2SO_4 .

To decompose the carbonate complex, add a 2 *M* solution of H_2SO_4 to the soda solution dropwise until the evolution of CO_2 stops. Precipitate the U^{VI} from the sulphuric acid solution with NH_4OH .

(b) Separation of Uranium Compounds with the Aid of Ion Exchangers

Fill the 50-ml burette with the resin AV-17 (see Experiment 3.1, Vol. 1). Pass a 1 *M* solution of NH_4NO_3 containing HNO_3 (0.1 *N*) through the resin.

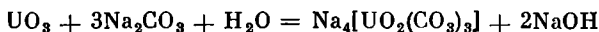
Dilute the solution obtained after the acid processing of the uranium ore with water to a pH of 1. Pass the diluted solution through a column at a rate of 2 ml/min. Collect the emerging solution in 50-ml portions. Determine the presence of U^{VI} qualitatively in each portion. (Add Na_2CO_3 and H_2O_2 . A brown colour of the solution after separation of the precipitate indicates that uranium compounds are present.)

The detection of U^{VI} in the emerging solution indicates the saturation of the resin with complex uranyl compounds. Regenerate the resin by treatment with a 1 M solution of NH_4NO_3 containing HNO_3 . Perform desorption (regeneration) at the same rate (2 ml/min) as adsorption. The resin treated in this way can be used again for sorption of the U^{VI} compounds.

By adding ammonia to the solution obtained after desorption, separate the uranium in the form of ammonium diuranate, and then transform it by roasting into uranous-uranic oxide.

B. CARBONATE METHOD

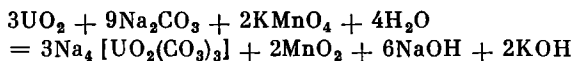
The processing of uranium minerals with soda solutions is based on the formation of the well soluble complex compound of U^{VI} :



The carbonate method is not used for decomposing sparsely soluble ores containing oxides of Ti, Ta, Nb, Th, and the rare-earth elements.

Primary minerals such as uraninite (pitchblende) are leached out in the presence of oxidizing agents, most frequently air or oxygen. Potassium permanganate ($KMnO_4$) is an effective oxidizing agent.

The process can be represented as follows in this case:

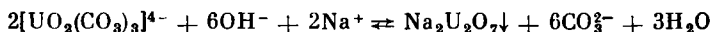


Uranovanadium carnotite ores are usually roasted in a mixture with sodium chloride prior to soda decomposition to transfer the vanadium compounds into a soluble form. The uranium from carnotite minerals is extracted into the solution sufficiently completely and without preliminary roasting.

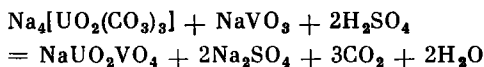
Leaching solutions containing sodium carbonate and bicarbonate simultaneously are employed in practice to prevent the precipitation of sodium diuranate at the expense of the forming alkali. In soda leaching, the uranium is separated from a number of accompanying impurities already at this stage of breaking down uranium ore.

Uranium compounds are separated from carbonate solutions by precipitation or adsorption.

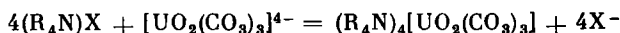
Upon treatment with sodium hydroxide, the uranium precipitates in the form of sodium diuranate:



If the soda solution also contains vanadium and the ratio $\text{V}_2\text{O}_5 : \text{UO}_2 = 1 : 2$ or more, sodium uranylvanadate is precipitated by neutralizing the solution with sulphuric acid to $\text{pH} = 6$:



The method of adsorption on anion-exchange resins can be used to recover uranium from solutions with a low uranium compound concentration, namely,



where X^- stands for the ions Cl^- or NO_3^- .

The carbonate complex is sorbed from the solution selectively.

The uranium compounds are washed out with a 1 *M* solution of NaCl or NaNO_3 containing Na_2CO_3 .

Equipment and Reagents

Equipment and Utensils. A water bath. A Kipp gas generator for preparing CO_2 . A porcelain beaker for 500 ml. A Büchner filter.

Radioactive Substances. Uranium ore (minerals that are titanotantaloniobates of rare-earth metals are not suitable).

Reagents. KMnO_4 . Solutions: 10% Na_2CO_3 ; 20% NaOH .

Performance of Work

Place a triturated weighed sample of uranium ore (200 g) into the porcelain beaker and add with stirring 300 ml of a solution of Na_2CO_3 saturated at room temperature with KMnO_4 .

Heat the mixture on the water bath, stirring it with a stream of CO_2 during three hours. Next separate the solution from the dry residue with the aid of a fluted filter. Wash the residue several times with small portions of a 10% hot solution of Na_2CO_3 .

Add a 20% solution of NaOH (~ 50 ml) to the filtrate heated on the water bath with stirring. Separate the precipitated sodium diuranate on the Büchner filter, wash it with a solution of NaOH , dry in a drying cupboard, and weigh it.

C. COMPLEXON-PHOSPHATE METHOD OF SEPARATING U^{VI} COMPOUNDS IN THE ANALYSIS OF ROCK AND MINERALS

The method is based on the separation of uranium in the form of uranyl phosphate with the use of a titanium salt as a coprecipitant. To prevent the precipitation of phosphates of other elements (Fe , Al , Cr , Cu , Ni , rare-earth elements, etc.), the disodium salt of ethylenediaminetetraacetic acid (Na-EDTA) is introduced into the solution. The introduction of trilon B makes it possible to combine the operation of separating the U^{VI} from the main hindering elements— Fe^{III} , Al^{III} , Cr^{III} , Cu^{II} , Ni^{II} , rare-earth elements, etc.—with its simultaneous separation from V^{III} , Mo^{VI} , and Cr^{VI} , which considerably simplifies the procedure of determination in objects having a complicated composition. Separation terminates in treatment of the precipitate with a solution of Na_2CO_3 , the uranium passing into the solution in the form of a carbonate complex.

The method is suitable for determining 0.001-2% of uranium in rock and minerals, is widely used in practice, and ensures the obtaining of reliable results.

Equipment and Reagents

Equipment and Utensils. An analytical balance. Beakers for 100 ml (2). A measuring cylinder for 50 ml. A watch glass. A funnel. A crystallizer. Measuring flasks for 25 ml (2).

Radioactive Substances. Uranium ore.

Reagents. NH_4NO_3 . Charcoal. Solutions: HCl with a density of 1.19 g/cm^3 ; 30% H_2O_2 ; H_2SO_4 (1:1); HNO_3 with a density of 1.4 g/cm^3 ; 10% Na_2HPO_4 ; 2% NH_4NO_3 ; 10% Na-EDTA ; 10% Na_2CO_3 ; TiOSO_4 with a TiO_2 concentration of about 5 mg/ml; 2% NH_4OH ; 0.1% methyl red.

Performance of Work

Place a weighed sample of the ore being analysed (0.5 g with a uranium content of 0.01%) into a 100-ml beaker and add 15-30 ml of hydrochloric acid (with a density of 1.19 g/cm^3) and 3-4 ml of perhydrol. Cover the beaker with the watch glass, boil the mixture on a small flame for 30-40 min. Cool the solution slightly, add 2-3 ml more of the perhydrol and 5 ml of hydrochloric acid, boil for 15 min, add 30 ml of hot water, and, covering the beaker with the watch glass, heat up to boiling point to dissolve the salts. Filter off the undissolved residue through a small pore-size filter, wash the residue several times with dilute hydrochloric acid, then two or three times with hot water in 10-ml portions and discard it.

Use treatment with a mixture of sulphuric and nitric acids for rock difficult to decompose with a mixture of hydrochloric acid and perhydrol (rock containing zirconium, tantaloniobium ores, etc.). For this purpose, add to the weighed sample of the ore being analysed 15 ml of sulphuric acid (1 : 1) and 5 ml of nitric acid (density 1.4 g/cm^3). Cover the beaker with the watch glass and heat it up to the evolution of H_2SO_4 vapour, then continue the heating another 40-60 min. Next remove the glass and heat the solution up to the removal of the major part of the sulphuric acid (until white vapour stops evolving). After cooling, add 10-15 ml of hydrochloric acid (density 1.19 g/cm^3) and 30-50 ml of water to the residue, boil the mixture, and filter off the undissolved residue as indicated above.

Add 2-3 g of NH_4NO_3 , 10-30 ml of a 10% solution of Na-EDTA (with a weighed sample of 0.2 g take 10 ml of the Na-EDTA solution, with a sample of 0.5 g—15 ml, and with one of 1-2 g—25-30 ml; a large surplus of Na-EDTA prevents the following precipitation of the phosphates) to the filtrate, whose volume is 80-100 ml, and neutralize it with NH_4OH according to methyl red (an external indicator). In the presence of Fe^{III} , establish the termination of neutralization according to the appearance of a red colour when the NH_4OH is added to the solution. Add another 1-2 drops of a 25% NH_4OH solution to the solution, heat up to boiling, and boil for two or three minutes. Boiling of the solution also facilitates the formation of complexonates of certain other metals.

Cool the solution in a crystallizer with cold water, add 10 ml of a 10% solution of Na_2HPO_4 [or $(\text{NH}_4)_2\text{HPO}_4$], 5 ml of a solution of TiOSO_4 as the coprecipitant, and neutralize with NH_4OH according to the methyl red indicator with the addition of one or two drops as a surplus of a 2% solution of NH_4OH .

Let the solution with the precipitate stand overnight, next filter off the precipitate through two medium pore-size paper filters inserted into each other, wash them on the filter with a hot 2% solution of NH_4NO_3 from 10 to 12 times in 5-7-ml portions without transferring the precipitate to the filter completely. At a Cr^{III} content over 50 mg, reprecipitate the precipitate of the phosphates with the addition of Na-EDTA.

Rinse the washed precipitate with hot water from the filter into the beaker in which precipitation was performed and add a 10% solution of Na_2CO_3 up to a concentration of 5% in the final solution.

Cover the beaker with the watch glass, heat the solution up to boiling, and evaporate it to a volume of 30-40 ml. When boiling, it is good practice to add about 0.1 g (on the tip of a spatula) of charcoal that facilitates the elimination of a foreign colour. After cooling the solution, transfer it together with the precipitate into a 25-ml measuring flask, dilute it with water up to the mark, and shake the flask. Filter off the precipitate through a filter preliminarily wetted with a solution of Na_2CO_3 , gathering the filtrate into a 100-ml beaker. Add nitric acid up to $\text{pH} = 1-2$ to the filtrate and evaporate until dry. Again treat the dry residue with nitric acid and add water until the salts dissolve. Transfer the solution to a 25-ml measuring flask and dilute it with water up to the mark.

Determine the uranium content in the solution by one of the photometric methods.

D. EXTRACTION DIETHYLDITHIOCARBAMINATE-COMPLEXON METHOD OF SEPARATING URANIUM

It is good to use this method for analytical purposes. It consists in using chloroform, diethyl ether, isoamyl alcohol, ethylacetate or amylacetate to extract uranium compounds with sodium diethyldithiocarbamate from a neutral solution ($\text{pH} = 6.5-7.5$) and in reextraction of the uranium com-

pound with an aqueous solution of $(\text{NH}_4)_2\text{CO}_3$. After decomposition of the uranium carbonate complex, the determination of uranium is completed with the aid of any photometric method.

Most hindering elements are masked by Na-EDTA. In the presence of Na-EDTA, compounds of Fe, Co, Ni, In, Ga, Zn, Pb, V, Nb, and Sn, which form stable soluble complexonates in a weakly acidic or neutral medium, are not extracted. Compounds of Be, Sb, Ti, and in part Mn, which in the conditions of the experiment do not form stable complexonates, may precipitate upon the neutralization of the solution.

Compounds of Cu, Ag, Bi, Hg, Tl, As, Se, and Te are extracted in the form of diethyldithiocarbaminates together with the uranium. But when the extract is treated with a solution of $(\text{NH}_4)_2\text{CO}_3$, only U^{VI} , which forms a more firmly bound carbonate complex in comparison with the diethyldithiocarbamate one, passes into the water layer.

Equipment and Reagents

Equipment and Utensils. A microbalance. A sand bath. Beakers for 250 and 100 ml. A measuring cylinder for 50 ml. Separatory funnels for 250 ml (2) and 50 (ml) 1. A measuring flask for 25 ml.

Radioactive Substances. Uranium ore.

Reagents. Chloroform. Solutions: NH_4OH (1 : 1); 10% Na-EDTA; 2% $(\text{C}_2\text{H}_5)_2\text{NC(S)SNa} \cdot 3\text{H}_2\text{O}$; 2% NH_4OH ; saturated $(\text{NH}_4)_2\text{CO}_3$.

Performance of Work

Decompose a weighed sample of the ore containing 10-50 mg of uranium in a suitable way. Add ammonia (1 : 1) to the transparent acid solution with a volume of about 50 ml obtained after decomposition of the ore until it becomes slightly turbid ($\text{pH} = 2.5-3$). Next add 10 ml of a 10% solution of Na-EDTA (for ores rich in iron increase the volume of the added Na-EDTA from 1.5 to 2 times). Neutralize the solution with NH_4OH (1 : 1) to a pH of 6.5-7.5 (according to litmus paper), and transfer it into a 250-ml separatory funnel. Add 5 ml of a 2% solution of sodium diethyldithiocarbamate to the solution, shake it, introduce 5-7 ml of chloroform, and extract the formed carbaminates during one or two minutes. Pour off the organic layer into the other separatory funnel, add 2 ml of a solution of sodium diethyldithiocarbamate and 5 ml of chloroform to the aqueous phase, and

extract again during one or two minutes. Repeat the extraction until a colourless layer of a new portion of chloroform is obtained when a carbamate is introduced. Discard the aqueous layer.

Combine all the portions of the chloroform, add to them 2 ml of a 2% solution of NH_4OH , 5-6 drops of a saturated solution of $(\text{NH}_4)_2\text{CO}_3$ and vigorously shake the mixture for two or three minutes in the 50-ml separatory funnel. Pour the aqueous layer into a 50-ml beaker, and treat the organic phase once more with NH_4OH and $(\text{NH}_4)_2\text{CO}_3$. Evaporate the aqueous solution containing the uranium compounds till dry in a beaker on the sand bath, treat it with dilute HNO_3 , again evaporate it till dry, dissolve the residue in water acidified with HNO_3 , transfer it to the 25-ml measuring flask, and take an aliquot part for determining the uranium content.

Experiment 11.2. QUANTITATIVE DETERMINATION OF URANIUM [6-14]

A. WEIGHT METHOD OF ANALYSIS WITH 8-HYDROXYQUINOLINE

In definite conditions, 8-hydroxyquinoline ($\text{C}_9\text{H}_6\text{NOH}$) precipitates the ions of many metals. By selecting various masking substances and the values of the pH, however, the precipitation of the uranium can be made selective. The method of determining uranium is based on the precipitation of uranyl 8-hydroxyquinolate in the presence of Na-EDTA that masks the accompanying elements.

The method can be employed for determining uranium in the presence of Th, Zr, the rare-earth elements and phosphites and for separating uranium from vanadium.

Equipment and Reagents

Equipment and Utensils. An analytical balance. A drying cupboard. A beaker for 250 ml. A glass filtering crucible No. 3.

Radioactive Substances. A solution containing U^{VI} , Th, and rare-earth elements.

Reagents. Solutions: 10% Na-EDTA; 0.01% and 4% ethanol $\text{C}_{10}\text{H}_8\text{NOH}$; 20% $\text{NH}_4\text{CH}_3\text{COO}$; CH_3COOH (1 : 1); 4 M NH_4OH ; 0.1% ethanol methyl red; H_2SO_4 with a density of 1.84 g/cm³; HCl with a density of 1.17 g/cm³; HNO_3 with a density of 1.4 g/cm³. Thymol blue.

Performance of Work

*(a) Determination of U^{VI} in the Presence of Th^{IV} , Rare-Earth Elements, and Zirconium **

To a solution containing 20-50 mg of uranium, and also thorium (not over 100 mg), rare-earth elements (not over 100 mg) and zirconium (not over 100 mg), add 10 ml of a 10% solution of Na-EDTA, neutralize with a 4 M solution of NH_4OH until a yellow colour appears according to methyl red, add 1.1 ml of acetic acid (1 : 1), 25 ml of a 20% solution of NH_4CH_3COO , dilute with water to 150-175 ml, and heat on a sand bath up to 70 °C. Add 5 ml of a 4% ethanol solution of 8-hydroxyquinoline to the solution dropwise with stirring (add 6-7 ml with a considerable zirconium content), place the mixture on a water bath, and hold it for 5 min at 30 °C. Filter off the precipitate through the glass crucible with a porous bottom No. 3, wash it with an 0.01% ethanol solution of 8-hydroxyquinoline, dry it at 110 °C until its mass is constant, and weigh the residue. The factor for reducing to uranium is 0.3386.

(b) Determination of Uranium in the Presence of Thorium, Rare-Earth Elements, and Phosphates

To a solution containing 40 mg of uranium, and also rare-earth elements (not over 30 mg), thorium, and phosphates (not over 2.5-fold amounts), add 2 ml of sulphuric acid with a density of 1.84 g/cm³, dilute with water to a volume of 125 ml, add 10 ml of a 10% solution of Na-EDTA, 7.5 ml of a 4% ethanol solution of 8-hydroxyquinoline, heat to 70 °C, neutralize the solution with a 4 M solution of NH_4OH according to thymol blue, add 25 ml of a 20% solution of NH_4CH_3COO , and further proceed as described in determining uranium in the absence of phosphates.

* When determining uranium by this method in the presence of 2.5-fold amounts of rare-earth elements, thorium, or zirconium, the error does not exceed 0.2-0.5%.

The error in determination does not exceed 0.4%; the method is not suitable for determining uranium with the simultaneous presence of zirconium and phosphates.

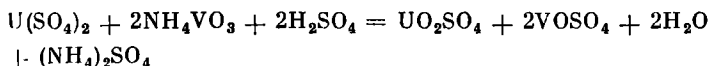
(c) Determination of Uranium in the Presence of Vanadium

To the solution being analysed containing about 40 mg of uranium and not over 100 mg of vanadium (reduced to V_2O_5) add nitric acid with a density of 1.4 g/cm^3 to prevent precipitation of the vanadic acid, neutralize with a 4 *M* ammonia solution up to the beginning of precipitation, add 0.4-0.5 ml of hydrochloric acid with a density of 1.17 g/cm^3 , dilute with water to 75 ml, add 10 ml of a 10% solution of Na-EDTA, and boil for 10-12 min. The solution will gradually turn blue owing to the reduction of the vanadium(V) to vanadium(IV). Neutralize the solution with a 4 *M* solution of NH_4OH using methyl red, add 1.1 ml of acetic acid (1 : 1), 25 ml of a 20% solution of NH_4CH_3COO , dilute with water to 150-175 ml, heat to $70^\circ C$, add 5 ml of a 4% ethanol solution of 8-hydroxyquinoline dropwise, and proceed as described when determining uranium in the presence of thorium and rare-earth elements.

The error in determining uranium in the presence of 2.5-fold amounts of vanadium (reduced to V_2O_5) does not exceed 0.2%.

B. VANADATOMETRIC DETERMINATION OF URANIUM

The method is based on the titration of U^{IV} with ammonium vanadate NH_4VO_3 in the presence of phenylanthranilic acid as an indicator:



The oxidation of U^{IV} occurs more rapidly in solutions of 3 *M* (and more concentrated) sulphuric acid, therefore direct titration with dilute (0.001 *N*) vanadate solutions is possible. For a sharper change in the colour at the end point, phosphoric acid is introduced into the solution being analysed prior to titration to accelerate the oxidation of the phenylanthranilic acid by the vanadate.

All the uranium is preliminarily transformed into U^{IV} . For this purpose, the U^{VI} is reduced in a reducer filled with electrolytically reduced cadmium. A small amount of U^{III} forms that is readily oxidized to U^{IV} . Such elements as Fe^{III} , Ti^{IV} , Mo^{VI} , V^V , and Nb^V are reduced together with the U^{VI} . It is therefore best of all to determine uranium in pure solutions after its separation from the hindering elements.

Equipment and Reagents

Equipment and Utensils. A cadmium reducer. A measuring flask for 50 ml. A pipette for 15 ml. A conical flask for 250 ml.

Radioactive Substances. A 0.03 M solution of UO_2SO_4 .

Reagents. Electrolytically reduced metallic cadmium (for filling the reducer). Solutions: 0.2; 1 N , 3 M H_2SO_4 and H_2SO_4 with a density of 1.84 g/cm³; 0.01 M NH_4VO_3 ; H_3PO_4 with a density of 1.6 g/cm³; 0.4% phenylanthranilic acid in a 0.4% solution of Na_2CO_3 .

Performance of Work

Dilute the initial solution of UO_2SO_4 with water in the 50-ml measuring flask up to the mark. Dilute an aliquot part of the solution (15 ml) containing 5-20 mg of uranium with an equal volume of a 3 M solution of H_2SO_4 to create a 1.5 M acidity. Wash the cadmium reducer with 1 N sulphuric acid and pass the solution (1.5 M with respect to H_2SO_4) to be analysed through it three or four times at a rate of 1-2 drops per second. Upon termination of the reduction, wash the reducer twice with 20 ml of 1 N sulphuric acid and twice with 10 ml of 0.2 N sulphuric acid.

When washing the reducer and during the reduction process, never allow the cadmium layer to become uncovered, because if it does, air will penetrate into it and complete reduction of the uranium will not be achieved in the following.

Collect the solution containing the reduced uranium in the 250-ml conical flask, introduce sulphuric acid with a density of 1.84 g/cm³ up to a concentration of 5-6 M (40-45 ml), 5 ml of phosphoric acid with a density of 1.6 g/cm³, and 5-6 drops of a solution of phenylanthranilic acid.

After thorough cooling, slowly titrate the solution with an 0.01 M solution of NH_4VO_3 until the greenish colour from one drop of the vanadate solution changes to a stable cherry-red colour.

Repeat the reduction and titration until converging results are obtained. 1 ml of a 0.0200 *N* solution of NH_4VO_3 is equivalent to 2.3807 mg of uranium.

C. COMPLEXONOMETRIC DETERMINATION OF U^{IV}

Uranium(IV) forms a stable complex compound with Na-EDTA at a molar ratio of 1 : 1 with a stability constant of 4.2×10^{25} ($\log K = 25.6$). This made it possible to develop a method of complexonometric titration of U^{IV} at $\text{pH} = 1.7 \pm 0.1$ with the use of arsenazo I as an indicator. The UO_2^{2+} is preliminarily reduced with formamidinesulphinic acid [$\text{H}_2\text{NC}(\text{NH})\text{SO}_2\text{H}$].

At the final point of titration, the colour of the solution changes from blue characteristic of the compound of U^{IV} with arsenazo I to pink characteristic of a solution of arsenazo I. The method can be used for determining uranium in alloys with Mg, Al, Fe, and Si, in technical salts (nitrates, sulphates, fluorides, acetates, oxalates, etc.), oxides, and production solutions.

Equipment and Reagents

Utensils. A conical flask for 250 ml. A pipette for 15 ml. A measuring flask for one litre.

Radioactive Substances. $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$.

Reagents. Solutions: 0.01 *M* Na-EDTA (3.7225 g of the air-dry salt $\text{C}_{10}\text{H}_{14}\text{O}_6\text{N}_2\text{Na}_3 \cdot 2\text{H}_2\text{O}$ are dissolved in water and diluted up to one litre with water; 1 ml of the solution of Na-EDTA is equivalent to 2.3807 mg of U); 0.05% arsenazo I; freshly prepared 0.68% formamidinesulphinic acid in 0.25 *N* H_2SO_4 ; 0.1% thymol blue in 5% ammonia; NH_4OH (1 : 5).

Performance of Work

From 50 ml of a solution containing 40-100 mg of U^{VI} , take 15 ml with the pipette and transfer to the 250-ml flask, add two or three drops of a 0.1% solution of thymol blue in NH_4OH (1:5) up to a pH of 2.5-2.7. Next add 30 ml of a 0.66% solution of formamidinesulphinic acid in 0.25 *N* sulphuric acid and heat at a temperature close to the boiling point (96-98 °C) for another 5 min. Dilute the solution with 175 ml of water, introduce 2 ml of a 0.05% solution of arsenazo I and titrate with a 0.01 *M* solution of Na-EDTA until the blue colour turns pink from one drop of the reagent.

Deviation of the pH of the solution being titrated from the indicated value makes it difficult to determine the end point of titration because of the indistinct colour change of the indicator.

D. COMPLEXONOMETRIC DETERMINATION OF U^{VI}

The uranyl ion forms with 1-(pyridyl-2'-azo)-2-naphthol $C_5H_5NN_2C_{10}H_7OH$ a red-violet compound with the maximum absorption of light at 560 nm. In definite conditions, the stability of this compound is less than that of the corresponding ethylenediaminetetraacetate (EDTA), as a result of which titration of the uranyl ion with Na-EDTA within the pH interval from 4.4 to 4.6 is possible in the presence of 1-(pyridyl-2'-azo)-2-naphthol as an internal indicator. The reaction proceeds slowly, therefore the solution must be heated to 80 °C. Owing to the low solubility of the compound of UO_2^{2+} with the indicator and of the indicator itself in water, an organic solvent is added—ethyl (50% by volume) or isopropyl (2 volumes per volume of solution) alcohol. The error in determination is ± 0.3 mg of uranium. It is best of all to use the method for determining uranium in pure solutions of its salts.

Equipment and Reagents

Utensils. A conical flask for 250 ml. A measuring cylinder for 50 ml. A burette for 25 ml.

Radioactive Substances. $UO_2(NO_3)_2 \cdot 6H_2O$.

Reagents. Isopropyl alcohol. Solutions: 0.2 *N* HNO_3 ; 25% urotropin; 0.01 *M* Na-EDTA; 0.1% methanol 1-(pyridyl-2'-azo)-2-naphthol.

Performance of Work

Acidify a solution (50 ml) containing 10-30 mg of U^{VI} with 0.2 *N* nitric acid to pH = 2-3, introduce 2 ml of a 25% solution of urotropin, add a double volume of isopropyl alcohol, heat until water vapour appears (80-90 °C), and introduce two or three drops of a 0.1% solution of 1-(pyridyl-2'-azo)-2-naphthol. Titrate the bright red solution with a 0.01 *M* solution of Na-EDTA until the solution's colour changes to purely yellow from one drop of the reagent solution.

E. PHOTOMETRIC DETERMINATION OF UIV WITH ARSENAZO I

Uranium(IV) forms a blue-violet complex compound having its maximum light absorption at 555 nm with arsenazo I in an acid medium (mineral acids). In this region of the spectrum, the solution of the reagent absorbs almost no light. The compound is quite stable, its instability constant is 6×10^{-17} . It is best of all to perform the determination at $\text{pH} = 1.5\text{--}1.8$; such an acidity is high enough to ensure selectivity because Fe^{II} , Be^{II} , Al^{III} , and rare-earth elements in these conditions do not react with arsenazo I. Among the reducing agents, it is convenient to use KI in an acid medium.

Equipment and Reagents

Equipment and Utensils. A spectrophotometer SF-4. Beakers for 50 ml (5). Measuring flasks for 25 ml (6).

Radioactive Substances. A solution of $\text{UO}_2(\text{NO}_3)_2$ containing 10 $\mu\text{g}/\text{ml}$ of U.

Reagents. Solutions: 10% KI; HCl (distilled) with a density of 1.19 g/cm^3 and 0.1 N; 0.5% arsenazo I; 0.002% $\text{Na}_2\text{S}_2\text{O}_3$.

Performance of Work

Pour 2, 4, 6, 8, and 10 ml of a standard solution of $\text{UO}_2(\text{NO}_3)_2$ into the five 50-ml beakers. Next add to each of the beakers 2 ml of the distilled hydrochloric acid, 0.8 ml of a 10% solution of KI, and evaporate until dry on a water bath. After cooling, introduce into each beaker 10 ml of 0.1 N hydrochloric acid, carefully (dropwise) add a 0.002% solution of $\text{Na}_2\text{S}_2\text{O}_3$ until the colour of iodine disappears, trying not to add more than 2-3 drops of excess thiosulphate. Introduce 2 ml of a 0.05% solution of arsenazo I, transfer the solutions into 25-ml measuring flasks and dilute them with water up to the mark. Prepare a control solution in a similar way. Measure the optical density.

F. EXTRACTION-PHOTOMETRIC DETERMINATION OF UVI WITH ARSENAZO III

The uranyl ion UO_2^{2+} forms a green complex compound having its maximum light absorption at 655 nm with arsenazo III. The sensitivity of determination is 0.01-0.02 μg

of uranium, and the molar extinction coefficient calculated from the photometric titration curve is 75 500. It is best to determine uranium at a pH of 1.7-2.5. The determination is not hindered by sulphate, fluoride, oxalate, and phosphate ions; it is hindered only by Th, Zr, Al, Cr^{III}, and rare-earth elements, but they can be masked by introducing suitable substances (sulphosalicylic acid in 0.05 *N* hydrochloric acid for aluminium, oxalic acid for zirconium and hafnium, etc.).

By reducing the UO_2^{2+} to U^{IV} , we can sharply increase the selectivity of determination, performing it in 5-6 *M* hydrochloric acid in the presence of oxalic acid. It is best of all to use granulated zinc in the presence of ascorbic acid as the reducing agent.

The extraction-photometric variant of determining U^{VI} is based on the ability of its compound with arsenazo III to be extracted by butanol from solutions containing Na-EDTA and diphenylguanidium chloride. The determination is not hindered by chlorides, nitrates, or fluorides (with a content up to 1 mg); sulphate and phosphate ions are precipitated by diphenylguanidium chloride. The precipitates formed in this case are separated by filtration of the extracts. The influence of thorium is eliminated by the addition of a fluoride (5 mg of KF per 5 ml of solution).

Equipment and Reagents

Equipment and Utensils. A Pulfrich photometer or a photoelectrocolorimeter. A water bath. Test tubes (6). Separatory funnels for 100 ml (6). A burette for 25 ml. A measuring cylinder for 10 ml.

Radioactive Substances. A solution of $\text{UO}_2(\text{NO}_3)_2$ containing 5 $\mu\text{g/ml}$ of U.

Reagents. Butanol. Solutions: 0.05 *N* HCl; 5% Na-EDTA; 0.05% arsenazo III; 20% diphenylguanidium chloride (mix about 105 g of the base diphenylguanidine with 80 ml of 3 *M* hydrochloric acid, dilute with water up to 500 ml; filter off the undissolved residue, and acidify the filtrate with a few drops of concentrated hydrochloric acid to a pH of 3-4).

Performance of Work

Pour a standard solution of $\text{UO}_2(\text{NO}_3)_2$ containing 10, 20, 30, 40 and 50 μg of U^{VI} into five test tubes, immerse the tubes into a boiling water bath, evaporate the solution until dry by passing air through it, and dissolve the residue

in 2.0 ml of 0.05 *N* hydrochloric acid. Introduce 2.5 ml of a 5% solution of Na-EDTA, 1.0 ml of a 0.05% solution of arsenazo III, 0.5 ml of a 20% solution of diphenyl guanidinium chloride, and 5.0 ml of butanol into the solution. Vigorously shake the tubes for 30 s, and after separation of the phases measure the optical density of the organic layer in a photometer or photoelectrocolorimeter relative to water.

The uranium in the specimen is determined similarly (after its decomposition in any suitable way)*.

G. PHOTOMETRIC DETERMINATION OF U^{VI} WITH 1-(PYRIDYL-2'-AZO)-RESORCINOL

One of the most sensitive reagents for the photometric determination of U^{VI} is 1-(pyridyl-2'-azo)-2,4-dihydroxybenzene, commonly known as 1-(pyridyl-2'-azo)-resorcinol (PAR). It reacts with UO_2^{2+} at pH = 3-10 to form a water-soluble compound in the proportion 1 : 1. The maximum light absorption of the solutions is at 510 nm. The sensitivity is 0.02 $\mu\text{g/ml}$ of uranium; optimal conditions are created at pH = 7.5 in the presence of a borate buffer solution. The Bouguer-Lambert-Beer law is observed within the interval of concentrations of 2-400 μg of U in 25 ml of solution. The determination of uranium is not hindered by the alkali and alkaline earth metals, Be^{II} , Ti^{IV} , Sn^{IV} , Mo^{VI} , Ir , W^{VI} , Rh , As^{III} , Se^{IV} , and Te^{IV} . It is hindered by Cu^{II} , Cr^{III} , Pb^{II} , Bi^{III} , Hg^{II} , Sb^{III} , Fe^{III} , and La^{III} that form precipitates in the conditions of determination, and also by Ni^{II} , Mn^{II} , Zr^{IV} , and Th^{IV} (a small amount, because a precipitate forms at a high thorium concentration) that form coloured compounds with PAR and do not react with Na-EDTA, except for manganese and zinc. Hence, the method of determining uranium with the aid of PAR can be used after its separation from the hindering ions.

In determining uranium by the complexon-phosphate or diethyldithiocarbamate-complexon method, the carbonate

* The uranium compound can be preliminarily extracted with a 20% solution of TBP in chloroform with the use of the TBP as a salting out agent and of Na-EDTA for retaining the hindering elements in the aqueous phase. Next the uranium can be reextracted with a solution of arsenazo III and determined by measuring the optical density of the aqueous phase.

complexes of uranium have to be preliminarily decomposed with hydrochloric or nitric acid, the solution must be evaporated to a small volume, a solution of urotropin must be carefully added up to a pH of 4-4.5, and then an aliquot part of the solution must be taken for analyses.

Equipment and Reagents

Equipment and Utensils. A Pulfrich photometer or a photoelectrocolorimeter. Measuring flasks for 25 ml (6).

Radioactive Substances. A solution of $\text{UO}_2(\text{NO}_3)_2$ containing 5 $\mu\text{g/ml}$ of U.

Reagents. Solutions: a borate buffer solution with a pH of 7.5 (dissolve 10.54 g of boric acid and 2.87 g of sodium tetraborate in water and dilute them with water up to one litre); 0.01% 1-(pyridyl-2'-azo)-resorcinol.

Performance of Work

Pour 2 ml of a 0.01% solution of 1-(pyridyl-2'-azo)-resorcinol into each of five 25-ml measuring flasks. Add 10 ml of the borate buffer solution, and then 1, 2, 3, 4, and 5 ml of the $\text{UO}_2(\text{NO}_3)_2$ solution so that the flasks contain 5, 10, 15, 20, and 25 μg of U, respectively, add another 5 ml of the borate buffer mixture to each flask, and dilute with water up to the mark. Stir the solutions well, and after choosing an appropriate light filter, measure the optical density in the Pulfrich photometer or the photoelectrocolorimeter relative to the solution of the reagent.

In a similar way, prepare solutions containing an unknown amount of uranium. Add an urotropin solution to acid solutions (up to a pH of 4-5), and then introduce the borate buffer solution.

Experiment 11.3. PREPARATION OF METALLIC URANIUM [15]

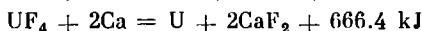
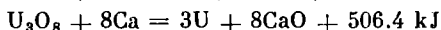
The high stability of uranium compounds (oxides, halides), and also the high reactivity of metallic uranium with respect to hydrogen, oxygen, nitrogen, water vapour, and carbon-containing compounds introduce complications into the process of its preparation. Uranium compounds with the elements listed above, however, do not dissolve in metallic uranium and can be separated already in the stages of reduc-

ing and refining melting when the process is performed in an atmosphere of inert gases or in a vacuum.

Compact uranium is a metal having a grey-steel colour. Uranium has three crystal modifications: rhombic—the α -form stable up to 668 °C, tetragonal—the β -form stable between 660 and 760 °C, and the γ -form stable above this temperature and having a body-centered cubic structure. When uranium is hardened (tempered), the β - and γ -modifications transform into the α -modification whose lattice parameters are $a = 0.2854$, $b = 0.5867$, and $c = 0.4957$ nm.

Metallic uranium can be prepared in two ways.

1. The Metallothermal Reduction of Uranium Oxides or Halides. Calcium or magnesium is customarily used as the reducing agent. The process of metallothermal reduction can be represented as follows:

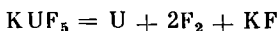


When UF_4 is reduced with metallic calcium, the liberated heat is sufficient for transferring the metallic uranium and slag into the molten state. After cooling, the uranium ingot separates quite well from the slag, which is a substantial advantage of the given method over other ones.

2. Electrolytic Reduction of Molten Uranium Halides:



or



The methods relating to the first group are the most applicable in laboratory conditions.

A. PREPARATION OF URANIUM BY REDUCING UO_2 WITH METALLIC CALCIUM AND CONTROL OF ITS PURITY

Equipment and Reagents

Equipment and Utensils. An analytical balance. A shaft electric furnace (for 1200 °C). A thermocouple with a pyrometer. An oil pump. An iron test tube (with a bore of 4 cm) hermetically closed with a cover having a branch pipe for evacuating air and filling with an inert gas. An iron test tube without a cover (bore 3 cm). A water bath. A beaker for 250 ml and two beakers for 100 ml. Porcelain crucibles (2).

Radioactive Substances. UO_2 .

Reagents. Argon in a cylinder. Solutions: 20% ethanol saturated with ammonium chloride; saturated NH_4Cl ; 96% ethanol; 30% HNO_3 ; 25% NH_3 (containing no CO_2); 3% NH_4NO_3 .

Performance of Work

Put the reaction mixture consisting of 3.5 g of UO_2 and 5.52 g of calcium (in the form of shavings) into the iron test tube without a cover. Place the tube with the mixture into the iron test tube with a cover, and close it tightly. Evacuate the air from the reaction space, and then fill it with argon. Heat the reaction mixture in the shaft furnace at 1000-1100 °C for three hours. After complete cooling, open the tube. Transfer its contents into the 250-ml beaker and treat them with a 20% solution of alcohol saturated with NH_4Cl . Add a small amount (10-15 ml) of a saturated aqueous solution of NH_4Cl to the mixture obtained. Separate the solution from the precipitate by decanting. Wash the precipitate consecutively with water and alcohol. Dry the product in the air.

Particles of metallic iron can be separated after drying with the aid of a magnet.

Determine the uranium content in the obtained powdery preparation. For this purpose, weigh a sample (~ 0.2 g) in a 100-ml beaker and dissolve it in 30% nitric acid taken in a small surplus. Precipitate ammonium diuranate from the obtained solution by adding (dropwise and with stirring) a 25% solution of NH_3 (without CO_2). Let the solution with the precipitate stand on the water bath for one hour. After this, filter off the precipitate with the aid of a smooth filter (small pore-size paper filter) and wash it with a 3% solution of NH_4NO_3 . Transfer the filter to a crucible, carbonize it on a burner, and next roast the substance in the crucible to a constant mass at a temperature of 800-850 °C. Weigh the obtained U_3O_8 on the analytical balance with an accuracy up to 0.0001 g.

Calculate the content of uranium in the preparation in per cent from two parallel analyses.

Investigate the purity of the uranium by X-ray techniques according to the powder method. Decipher the X-ray photograph and compare it with published data for the α -modification.

B. PREPARATION OF URANIUM BY REDUCING UF_4 WITH METALLIC CALCIUM AND CONTROL OF ITS PURITY

Equipment and Reagents

Equipment and Utensils. A crucible made from refractory steel lined with CaF_2 . A vacuum desiccator.

Radioactive Substances. UF_4 .

Reagents. Metallic calcium. CaF_2 . A magnesium ribbon. Argon in a cylinder.

Performance of Work

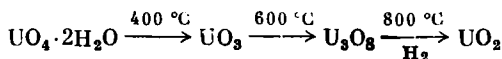
Thoroughly mix a weighed sample of UF_4 (20 g) with 6 g of freshly prepared shavings of metallic calcium. Put 5 g of CaF_2 , and then the reaction mixture, onto the bottom of the refractory steel crucible. Compact it with a pestle and insert the coiled magnesium ribbon into the centre of the mixture. Place the crucible with the mixture in the vacuum desiccator, evacuate the air with the aid of a water-jet pump, and then fill the desiccator with argon. The voids in the reaction mixture will become filled with the inert gas. Rapidly transfer the crucible from the desiccator into a fume cupboard and ignite the magnesium ribbon (with the aid of a burning splinter inserted into a long glass tube). After cooling, extract the regulus from the crucible and weigh it. Determine the yield of uranium (in %).

Investigate the purity of the obtained metallic uranium by X-ray techniques, comparing the Debye powder diagram with published data for the α -modification.

Experiment 11.4. PREPARATION OF OXYGEN URANIUM COMPOUNDS AND INVESTIGATION OF THEIR THERMAL STABILITY [2]

The compounds UO_2 , U_3O_8 , UO_3 , and $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ are the most important in uranium technology in the system uranium-oxygen, which has been studied in quite great detail to date. Uranium peroxide dihydrate $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ is often used for separating and purifying uranium. This compound is insoluble in acids, which makes it possible to separate uranium from a number of impurities remaining in an acid solution (Na, Mg, Ca, Al, rare-earth elements, Ti, Ni, Co,

Mn, Cu, and Cd). Uranium peroxide dihydrate may be used as the starting substance for preparing other oxygen compounds as follows:



A. URANIUM PEROXIDE HYDRATE, TRIOXIDE, AND URANOUS-URANIC OXIDE

Equipment and Reagents

Equipment and Utensils. A continuous weighing balance. A Kurnakov pyrometer. A crucible furnace. A centrifuge. A drying cupboard. Dropping funnels (3). A beaker for 500 ml. Wash bottles (2). A glass filter No. 3 or No. 4. A glass weighing bottle with a lid.

Radioactive Substances. A 10% solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

Reagents. Solutions: 3% H_2O_2 ; 3% NH_3 ; 40% NaOH .

Performance of Work

(a) Uranium Peroxide Hydrate

Pour 50 ml of distilled water into the 500-ml beaker. Add solutions of 10% $\text{UO}_2(\text{NO}_3)_2$ (200 ml), 3% H_2O_2 (100 ml), and 3% NH_3 to the beaker with water dropwise from three dropping funnels simultaneously. Stir the precipitate formed in the beaker using a stream of air or oxygen preliminarily passed through the two wash bottles containing a 40% solution of NaOH to remove CO_2 . Upon termination of the reaction, transfer the solution with the precipitate into centrifuge tubes. Separate the precipitate from the mother liquor, again add water, thoroughly stir, and centrifuge. Repeat the operation until the washing water contains no NO_3^- (a reaction with a sulphuric acid solution of diphenylamine). Suck off the washed product on a dense glass filter (No. 3 or 4) and dry in a drying cupboard at a temperature of 100-150 °C up to a constant mass.

Triturate the light yellow preparation of $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ in an agate mortar.

The uranium content in the substance obtained in per cent is determined by the method of "afterburning". Roast a weighed sample of the preparation (~0.2 g) in a stream of oxygen up to a constant mass at 800-850 °C. Use the amount of U_3O_8 obtained to calculate the uranium content in the initial specimen.

To investigate the thermal stability of the $\text{UO}_4 \cdot \text{H}_2\text{O}$, use the Kurnakov pyrometer to plot the heating curve of the peroxide hydrate in the air within the temperature range from 200 to 900 °C; determine the change in the mass depending on the heating temperature on the continuous balance. Use the data obtained to determine the composition and temperature conditions of formation of the decomposition products of $\text{UO}_4 \cdot 2\text{H}_2\text{O}$.

(b) Uranium Trioxide

Heat uranium peroxide hydrate (5 g) in the crucible furnace up to a constant mass at 350-400 °C in a stream of oxygen to avoid decomposition of the uranium trioxide. For this purpose, pass dry oxygen through the opening in the cover of the crucible furnace (this operation can also be performed in a tubular furnace).

Uranium trioxide is a reddish-orange hygroscopic powder. To prevent hydration of the uranium trioxide when weighing it, place the crucible with the preparation in a weighing bottle closed with a cover.

Perform chemical analysis of the UO_3 by the method of "afterburning" [see Section (a)].

(c) Uranous-Uranic Oxide

Heat uranium trioxide (3 g) in the air to a constant mass at 800-900 °C. The olive green (sometimes black green) product obtained is U_3O_8 —the most thermally stable uranium compound.

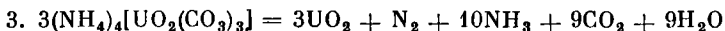
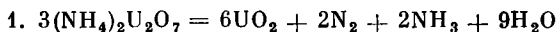
B. URANIUM DIOXIDE

Uranium dioxide is one of the most important uranium compounds. It is the starting substance in the production of UF_4 from which metallic uranium and UF_6 are produced. In addition, in some types of reactors, the dioxide is used as the nuclear fuel.

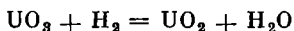
Uranium dioxide is a brown powder. Its density evaluated according to radiographic data is 10.96 g/cm³, and its melting point is 2860 ± 45 °C. Uranium dioxide has a face-centered cubic lattice and a structure of the fluorite type.

For stoichiometrically pure UO_2 , the lattice constant is 0.5460 nm.

Uranium dioxide can be obtained by heating, without the access of air, uranium compounds (ammonium diuranate, uranyl oxalate, and uranyl ammonium tricarbonat). When the latter decompose, gaseous products are evolved that have reducing properties:



Reduction of the higher oxides of uranium by hydrogen or other reducing agents (NH_3 , CO) also leads to the formation of UO_2 , for example:



Equipment and Reagents

Equipment and Utensils. A Kurnakov pyrometer. A continuous balance. Tubular electric furnaces (2). A thermocouple with a pyrometer. A Kipp gas generator. Quartz tubes 2-3 cm in diameter and 50-60 cm long (2). Wash bottles (4). Columns with P_2O_5 (2).

Radioactive Substances. Uranous-uranic oxide or uranium trioxide.

Reagents. Metallic copper (reduced). Concentrated H_2SO_4 .

Performance of Work

Assemble an arrangement for reduction with hydrogen and check its tightness. Clean the hydrogen prepared in the Kipp gas generator from impurities by passing it (consecutively) through two wash bottles with an acidified solution of potassium permanganate, a tube with reduced copper heated by an electric furnace (at 600°C), two wash bottles with 96% sulphuric acid, and columns filled with a mixture of glass wool and phosphoric anhydride. Only purified and dried hydrogen should enter the quartz tube placed in the furnace.

Place a weighed sample of U_3O_8 or UO_3 (~ 3 g) into a porcelain boat preliminarily brought up to a constant mass. Put the boat with the substance into a reaction tube, and again check the tightness of the arrangement. Test the purity of the hydrogen, fill the arrangement with the hydrogen, and only after this switch on the heating system.

Perform reduction at 800 °C during two hours. Cool the reduced product in a stream of hydrogen and weigh it. Repeat the heating in a hydrogen stream once more during one hour. Terminate the process when the mass of the substance remains constant.

Use the Kurnakov pyrometer to plot a curve of heating of the UO_2 in the air within a temperature range from 20 to 800 °C, and determine the change in the mass when heating on the continuous balance. Use the data obtained to determine the composition and temperature conditions of formation of the UO_2 oxidation products.

Prepare an X-ray photograph of the UO_2 , decipher it, and compare with published data.

Experiment 11.5. PREPARATION OF SULPHUR URANIUM COMPOUNDS AND THEIR ANALYSIS [3]

To date, the sulphides US , U_2S_3 , U_3S_5 , US_2 , and US_3 and the oxysulphides $\text{UO}_2 \cdot 2\text{US}_2$, UO_2S , and UOS have been described. The disulphide US_2 and the oxysulphide UOS are the most well known of them.

Most of the sulphur compounds are refractory substances having high values of their density and thermal conductivity in conditions of elevated temperatures, and also a small slow neutron capture cross section, a high mechanical strength, chemical inertness, and compatibility with a number of the materials employed in nuclear reactors. These properties make sulphur compounds of uranium prospective as materials for the manufacture of fuel elements.

A. URANIUM OXYSULPHIDE

The oxysulphide of the composition UOS has a blue black colour. Its lattice is tetragonal ($a = 0.3835 \pm 0.0002$ nm, $c = 0.6682 \pm 0.0002$ nm). Its calculated density is 9.60 g/cm³.

Equipment and Reagents

Equipment and Utensils. A tubular furnace (for 1200-1400 °C). A thermocouple with a pyrometer. A Kipp gas generator for preparing H_2S . A porcelain tube 80 cm long with a diameter of 2-3 cm. Wash bot-

bles (5). A bottle with a reducer. Columns with P_2O_5 (2). U-shaped tubes (2). A graphite boat.

Radioactive Substances. U_3O_8 .

Reagents. Amalgamated zinc. Bromine. CO in a gasometer. Pyrogallol. CCl_4 . Solutions: $CrCl_3$; concentrated HNO_3 , H_2SO_4 , HCl ; 5% $BaCl_2$.

Performance of Work

Assemble the arrangement (Fig. 11.1). Put a weighed sample of U_3O_8 (3-4 g) in a graphite boat into porcelain tube 9 heated by a tubular furnace for 1200-1400 °C. Dry the system during one hour at 300-400 °C in a stream of CO purified of oxygen traces. For this purpose, pass the CO from the gasometer through wash bottles 2 filled with a pyrogallol solution and wash bottles 3 filled with concentrated H_2SO_4 . Next pass a stream of H_2S purified and dried by consecutively passing it through bottle 6 with a $CrCl_3$ solution and columns (U-shaped tube) 8 with P_2O_5 from Kipp gas generator 4 into reaction tube 9. Raise the temperature of the furnace to 1050-1100 °C. At this temperature, the process goes on for 3-4 h, after which cool the arrangement in the stream of H_2S , and then in a stream of CO.

Determine the uranium and sulphur content in the preparation.

To perform the analysis, place the product (0.2 g) in a beaker and pour in 2 ml of a mixture of two parts of bromine and three parts of CCl_4 (by volume). Cover the beaker with a watch glass and let it stand for 15 min with stirring. Next add 10 ml of concentrated HNO_3 and again let it stand for 15 min (without heating). Transfer the beaker onto a water bath (on a thick layer of asbestos), and heat the mixture until the reaction stops and the major part of the bromine is removed. Take off the watch glass, wash with water, and evaporate the solution until dry. Dissolve the residue in a small amount of distilled water with heating.

To determine the uranium content, acidify the solution with nitric acid, and precipitate the uranium with ammonia (see Experiment 11.3A).

To determine the sulphur, evaporate the filtrate after separation of the uranium until dry on a water bath, and decompose the NO_3^- by heating three times with hydrochloric acid. Dissolve the dry residue in 150 ml of distilled water, add 1 ml of concentrated hydrochloric acid to the solution,

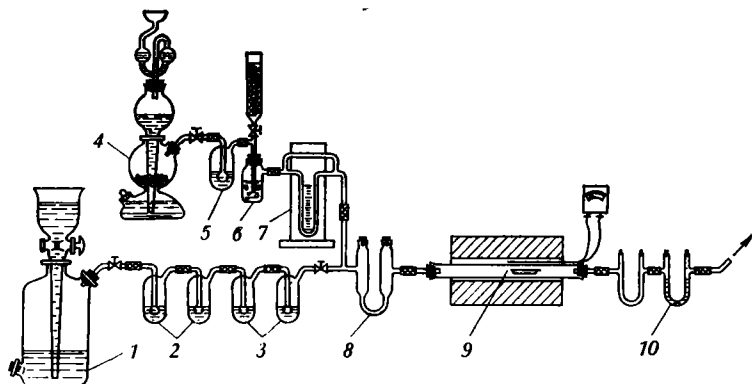


Fig. 11.1 Arrangement for preparing sulphur uranium compounds:

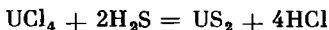
1—gasometer with CO; 2—wash bottles with alkaline solution of pyrogallol; 3—wash bottles with concentrated H_2SO_4 ; 4—Kipp gas generator for preparing H_2S ; 5—wash bottle with glycerin; 6—bottles with solution of CrCl_2 ; 7—manometer; 8—U-shaped tube with P_2O_5 ; 9—reaction tube; 10—U-shaped tube with CaCl_2 .

and then slowly pour in 10 ml of a 5% solution of BaCl_2 . Heat the beaker with the precipitate several hours on a water bath. Next filter off the precipitate, wash it several times with hot water, and roast it up to a constant mass at 900°C . Use the result obtained to calculate the sulphur content in the substance.

Prepare an X-ray photograph of the obtained oxysulphide, decipher it, and compare it with published data.

B. URANIUM DISULPHIDE

Uranium disulphide was first prepared by reacting metallic uranium with sulphur. This compound also forms when uranium tetrachloride is reacted with hydrogen sulphide:



A convenient way of preparing US_2 is to react uranium hydride with hydrogen sulphide:



The reduction of UO_2 or U_3O_8 with carbon in the presence of H_2S also leads to the formation of uranium disulphide. The reaction proceeds quite rapidly at $1200\text{--}1300^\circ\text{C}$. The

product obtained in these conditions, however, is contaminated with an admixture of the oxysulphide. The traces of oxygen can be removed only by multifold repetition of the process with the comminuted product.

Uranium disulphide forms black or steel gray crystals existing in three modifications: tetragonal—the α -form stable within the temperature range from 1350 to 1536 °C ($a = 1.025 \pm 0.005$, $c = 0.630 \pm 0.003$ nm), rhombic—the β -form stable below 1350 °C ($a = 0.422 \pm 0.002$, $b = 0.7108 \pm 0.004$, $c = 0.845 \pm 0.004$ nm), and hexagonal—the γ -form prepared by the action of dry H_2S on the sulphide of the composition U_3S_5 at 380-400 °C. At 425 °C, the γ -modification transforms into the β -modification.

Performance of Work

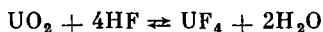
Assemble the arrangement (see Fig. 11.1). Put uranous-uranic oxide (3 g) into the graphite boat and the latter into the porcelain reaction tube heated by the tubular furnace for 1400 °C. After preliminary (for one hour) drying of the system at 200-400 °C in a stream of CO purified of oxygen traces and dried, raise the temperature of the furnace to 1350-1380 °C. In these conditions, pass purified and dried H_2S during 3-4 h through the reaction tube; for this purpose, first pass it through bottles with a solution of $CrCl_2$ and P_2O_5 . Next, without stopping the stream of H_2S , sharply lower the temperature in the furnace to 1000 °C and keep it in these conditions for another hour. When sharply cooled, the α -form of the uranium disulphide does not have time to transform into the β -form. Heating at 1000 °C makes it possible to prevent the contamination of the US_2 by lower sulphides that in these conditions add sulphur and transform into the disulphide. After cooling (first in a stream of H_2S , and then of CO), transfer the substance from the graphite boat to an agate mortar, thoroughly triturate it, again place it into the graphite boat, and repeat the entire process. Repeat trituration of the product and reduction twice.

Subject the substance obtained as a result of threefold reduction to chemical analysis (according to the procedure described in Experiment 11.5A). Prove the individuality of the substance by X-ray techniques. Decipher the obtained Debye powder diagram and compare it with published data for the α -modification of US_2 .

Experiment 11.6. SYNTHESIS OF ANHYDROUS URANIUM HALIDES [1, 4, 5]

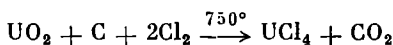
Uranium oxides can be used as the starting substances for preparing anhydrous UF_4 , UCl_4 , and UBr_4 ; the free metal and uranium hydride, carbide, nitride, and sulphide can also be used. It is most convenient, however, to use the reactive UO_2 prepared in conditions of low temperatures (500-700 °C).

In the synthesis of anhydrous UF_4 , either HF or NH_4HF_2 can be used as the fluorinating agent. The relevant hydrogen halides cannot be used to prepare UCl_4 and UBr_4 because at elevated temperatures the equilibrium of the reaction

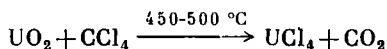


is virtually completely shifted to the left side. At low temperatures, the thermodynamic relations become favourable, but the process does not proceed to the end. For example, only UOCl_2 forms instead of UCl_4 .

It is the most convenient to prepare UCl_4 and UBr_4 by halogenation of the dioxide with free chlorine or bromine in the presence of substances having a high affinity to oxygen, for example, carbon:

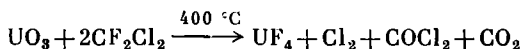


or by reacting UO_2 with CCl_4 :



Lowering of the temperature leads to a decrease in the content of the pentachloride in the UCl_4 .

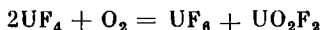
Freons (mixed fluoro- and chlorosubstituted hydrocarbons) are very effective fluorinating reducing reagents for preparing uranium tetrafluoride. No corrosion-proof apparatus is needed for the reaction. The reaction of UO_3 with Freon-12 proceeds as follows:



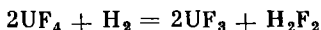
A. URANIUM TETRAFLUORIDE

Uranium tetrafluoride is a green, non-volatile, non-hygroscopic substance poorly soluble in water. Its melting point is $960 \pm 5^\circ\text{C}$.

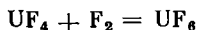
Uranium tetrafluoride has a low chemical activity. Heating in pure dry oxygen (800 °C) follows the reaction:



Pure hydrogen at 1000 °C reduces UF_4 :



Fluorine when slightly heated (below 250 °C) transforms the tetrafluoride into the hexafluoride:



Equipment and Reagents

Equipment and Utensils. A tubular electric furnace (for 600 °C). A quartz tube 60 cm long and 2-3 cm in diameter. Columns with P_2O_5 (3). A graphite boat.

Radioactive Substances. UO_3 .

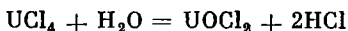
Reagents. Freon-12 (in a cylinder). Nitrogen (in a gasometer).

Performance of Work

Place a weighed sample of UO_3 (5 g) in the graphite boat into the quartz reaction tube inserted into the electric furnace. Connect the tube via a tee to the gasometer with nitrogen and the cylinder with Freon-12, installing three consecutively connected bottles with P_2O_5 between the tube and the sources of the gases. First pass dry nitrogen through the system for drying and for displacing the air. Next, without stopping the supply of nitrogen, raise the temperature in the furnace to 400 °C and with the aid of a reducer feed in Freon-12 from its cylinder. The Freon, like the nitrogen, must be preliminarily dried by passing it through bottles with P_2O_5 . Perform fluorination during two hours. After this, switch off the furnace and cool the system in the stream of nitrogen. Appraise the completeness of the reaction according to the change in the mass of the initial substance as follows from the above equation of the reaction.

B. URANIUM TETRACHLORIDE

Uranium tetrachloride is a dark green substance melting at 590 ± 1 °C and boiling at 792 °C. It is very hygroscopic. The absorption of water vapour is attended by the reaction



Aqueous solutions of UCl_4 have an acid reaction because of hydrolysis. At temperatures up to 230°C , UCl_4 is stable with respect to oxygen, but in an aqueous solution oxidation with the formation of UO_2^{2+} proceeds at an appreciable rate already at room temperature.

Equipment and Reagents

Equipment and Utensils. Tubular electric furnaces for 600°C (2). A dry chamber. A Kipp gas generator for preparing hydrogen. Quartz tubes 60 cm long and 2-3 cm in diameter (2). Wash bottles (4). A column with P_2O_5 . A Wurtz flask for 500 ml.

Radioactive Substances. UO_3 .

Reagents. Cu (reduced). CCl_4 dried over P_2O_5 . Nitrogen (in a gasometer). Solutions: KMnO_4 ; concentrated H_2SO_4 .

Performance of Work

Assemble the arrangement (Fig. 11.2). Clean the hydrogen produced by the Kipp gas generator from impurities by consecutively passing it through two wash bottles with an acidified solution of KMnO_4 , tube 4 with reduced copper heated by the furnace (600°C), two wash bottles 5 with 96% H_2SO_4 and through column 6 filled with a mixture of glass wool with P_2O_5 . The purified and dried hydrogen flows into quartz tube 8 placed in the furnace. Check the tightness of the arrangement.

Put a weighed sample of the UO_3 (5 g) in a porcelain boat into tube 8, and again check the tightness of the arrangement. Displace air from the system with a stream of hydrogen, passing it through the cold (!) arrangement, including flask 7. Having convinced yourself in the purity of the hydrogen (check it at the outlet from the system), turn cock *b* and direct the hydrogen into quartz tube 8, bypassing the flask with the CCl_4 . Switch on the heating system and perform reduction during three hours at 500°C . Next turn cock *a* to switch off the Kipp gas generator and connect the gasometer with nitrogen. After the complete displacement of the hydrogen from the arrangement, lower the temperature of the furnace to 450°C and feed CCl_4 vapour into the tube. For this purpose, turn cock *b* so that a weak stream of nitrogen, picking up CCl_4 vapour ($50-60^\circ\text{C}$), will enter the reaction tube. Perform the chlorination for three hours, after which cool the arrangement without stopping the

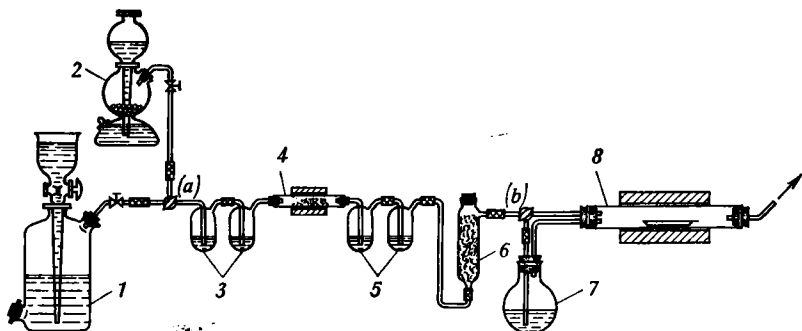


Fig. 11.2. Arrangement for preparing uranium tetrachloride: 1—gasometer with N_2 ; 2—Kipp gas generator for preparing H_2 ; 3—wash bottles with solution of $KMnO_4$; 4—tube with reduced copper heated by electric furnace ($600^\circ C$); 5—wash bottles with concentrated H_2SO_4 ; 6—column with P_2O_5 ; 7—flask with CCl_4 ; 8—reaction tube

passage of the nitrogen. Extract the boat with the substance from the quartz tube. Transfer the substance into a previously weighed weighing bottle in the dry chamber, weigh the preparation, and calculate the yield.

Active UO_2 , which is the starting substance for preparing UCl_4 , can also be obtained by decomposing $UO_2C_2O_4 \cdot 3H_2O$. In this case, the Kipp gas generator is excluded from the arrangement. Place uranyl oxalate trihydrate (7 g) in a porcelain boat into quartz tube 8. Displace air from the system with nitrogen, next, without stopping to feed in nitrogen, slowly raise the temperature of the furnace to $450^\circ C$ and maintain it at this value for two hours, after which feed CCl_4 vapour into the reaction tube. Determine the U : Cl ratio in the compound.

Dissolve a small amount of the preparation (about 0.5 g) in 50 ml of water, take 20 ml with a pipette and acidify with nitric acid (2-3 ml). Determine the uranium content in the solution (see Experiment 11.3A).

Use the same volume of the solution for determining chlorine. Dilute the solution with water up to 100 ml. Next, while stirring, add a 5% solution of $AgNO_3$ containing 1 ml of HNO_3 per litre of solution. Add the solution (gradually) up to coagulation and stopping of the formation of a precipitate. Avoid a large surplus of silver nitrate.

Heat the entire contents of the flask to about $60^\circ C$. Let the precipitate settle, and then add a few more drops of the

AgNO_3 solution. Repeat the operation if a precipitate appears. Upon completion of precipitation, put the flask in a dark spot for several hours, best of all overnight.

Pour off the transparent solution by decantation through a preliminarily weighed Gooch or Munroe crucible and wash the precipitate by decantation (0.05 g of AgNO_3 in 1 litre of the solution). Next wash it with a small amount of dilute HNO_3 (1:99), and then twice with water. First dry the crucible with its contents at a temperature of 100°C , then at $130\text{--}150^\circ\text{C}$, cool in a desiccator, and weigh. Use the data obtained to calculate the ratio $\text{U}:\text{Cl}$.

C. URANIUM TETRABROMIDE

Uranium tetrabromide is a crystalline substance whose colour varies from rust coloured to dark brown depending on the size of the crystals. The melting point of UBr_4 is $519 \pm 2^\circ\text{C}$, its boiling point is 761°C (with decomposition), it is hygroscopic and readily dissolves in water, appreciably hydrolyzing. In humid air, UBr_4 rapidly oxidizes to UO_2Br_2 .

Equipment and Reagents

Equipment and Utensils. Tubular furnaces (2). A thermocouple with a pyrometer. A quartz tube 60 cm long and 2-3 cm in diameter. Wash bottles (3). A column with P_2O_5 . An apparatus for bromination. A dry chamber.

Radioactive Substances. UO_2 (freshly prepared at $600\text{--}650^\circ\text{C}$).

Reagents. Reduced Cu. Dry bromine. Nitrogen (from a gasometer). Powdered charcoal.

Performance of Work

Perform bromination in a quartz arrangement (Fig. 11.3). Prepare a mixture of 2 g of UO_2 with 3 g of powdered charcoal, transfer the mixture into a porcelain boat, and pour a thin layer of the powdered charcoal over it. Place the boat into reaction tube 4. Dry the system at $200\text{--}300^\circ\text{C}$ during two hours with nitrogen that has been preliminarily purified of traces of oxygen and water vapour by passing it through a wash bottle with an alkaline solution of pyrogallol, a tube with reduced copper (at 600°C), two bottles with 96% sulphuric acid, and a column filled with a mixture of glass wool with P_2O_5 . Next direct the stream of dry nitrogen

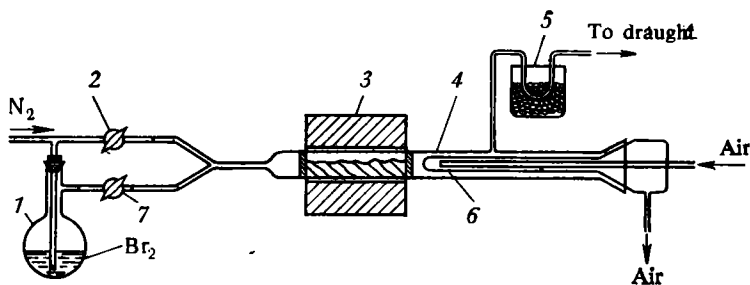


Fig. 11.3. Arrangement for preparing anhydrous uranium and thorium bromides:

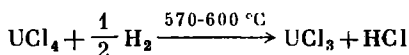
1—Wurtz flask with dry bromine; 2—cock controlling the nitrogen stream; 3—electric furnace (900 °C); 4—reaction tube; 5—bromine absorber; 6—quartz air cooler; 7—cock controlling the bromine stream

through a vessel containing bromine thoroughly dried over P_2O_5 , and feed the bromine by means of the nitrogen stream into the reaction tube.

Raise the temperature of the furnace to 800 °C and continue to pass the bromine vapour at this temperature through the arrangement during three hours. Next switch off the furnace, at 200 °C stop feeding in the bromine, and cool the arrangement to room temperature, passing nitrogen through it. Extract cooler 6 on which crystals of UBr_4 sublime from the reaction tube. Carefully transfer the substance obtained into a weighing bottle in the dry chamber. Coat the weighing bottle with paraffin. Use the insignificant amount of UBr_4 remaining on the tube for determining the ratio between the uranium and bromine (see Sec. B of the present experiment).

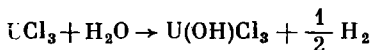
D. URANIUM TRICHLORIDE

This compound can be prepared by reacting uranium hydride with hydrogen chloride. But the most convenient method of preparing UCl_3 is the reduction of UCl_4 with hydrogen:



The UCl_3 is obtained in the form of dark red acicular crystals. Its melting point is 842 ± 5 °C. The substance is

hygroscopic; its aqueous solution is not stable because of oxidation by water:



Equipment and Reagents

Equipment and Utensils. Tubular furnaces for 600 °C (2). A dry chamber. A Kipp gas generator for preparing hydrogen. Quartz tubes 60 cm long and 2-3 cm in diameter (2). Wash bottles (4). A column with P_2O_5 . A Wurtz flask for 500 ml.

Radioactive Substances. UO_3 .

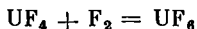
Reagents. Reduced Cu. CCl_4 . Nitrogen (from a gasometer).

Performance of Work

Prepare uranium tetrachloride according to the procedure described in Sec. B of the present experiment. Next reduce the UCl_4 with hydrogen in the same tube in which it was prepared. For this purpose, stop the supply of CCl_4 , cool the system in a stream of dry nitrogen purified of O_2 , and then pass hydrogen through. After thorough and repeated checking of the purity of the hydrogen (at the outlet from the arrangement), increase the furnace temperature to 575 °C, and in these conditions carry on reduction during two hours. Next raise the temperature to 650 °C and maintain it until the outgoing gases contain no HCl. Cool the arrangement in a hydrogen stream to room temperature. Transfer the substance into a weighing bottle in the dry chamber. Test the relation of the UCl_3 to water. Determine the ratio between U and Cl in the preparation (see Sec. A).

E. URANIUM HEXAFLUORIDE

The higher uranium fluoride is the only stable gaseous compound of uranium. It can be prepared by acting with fluoride on any uranium compound. Fluorination is performed most frequently with heating:



Owing to the strong corroding action of F_2 , however, this method is not convenient in laboratory conditions.

UF_6 can be prepared by oxidation with dry oxygen at 800 °C:



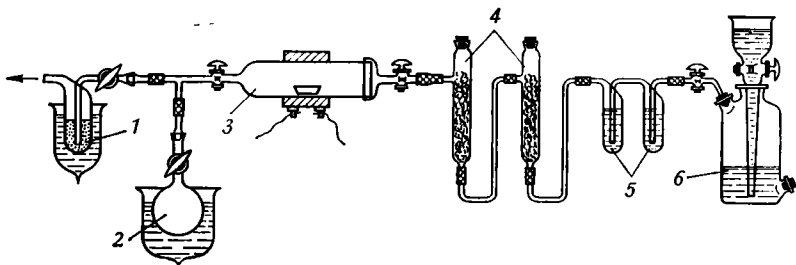
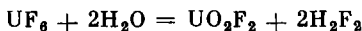


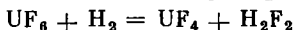
Fig. 11.4. Arrangement for preparing uranium hexafluoride:
 1—bottle with active charcoal cooled by liquid nitrogen;
 2—glass ampoule cooled by mixture of acetone with dry ice;
 3—reaction tube; 4—columns with P_2O_5 ; 5—wash bottles with concentrated H_2SO_4 ; 6—gasometer with O_2

UF_6 at room temperature is a colourless volatile substance forming transparent crystals melting at $64.02^\circ C$ (at $p = 1.47 \times 10^4$ Pa). At $56.5^\circ C$, the pressure of UF_6 vapour is 9.88×10^3 Pa.

Uranium hexafluoride is very reactive. It reacts vigorously with water:



reduces under the action of hydrogen and hydrogen halides:



and is a strong fluorinating agent. At elevated temperatures, it reacts with most metals. Aluminium, copper and nickel, owing to the protective film covering their surface, are the most resistant to UF_6 .

Equipment and Reagents

Equipment and Utensils. A tubular furnace. A thermocouple with a pyrometer. A nickel or copper tube 2-3 cm in diameter. A nickel boat. Wash bottles (2). A column with P_2O_5 (2). An ampoule of molybdenum glass.

Radioactive Substances. UF_4 .

Reagents. Acetone (or ether). Dry ice. Oxygen (in a gasometer).

Performance of Work

Assemble the arrangement (Fig. 11.4). Place anhydrous UF_4 (5 g) in the nickel boat into nickel tube 3. Dry the system for one hour with a stream of dry oxygen supplied

from gasometer 6 through wash bottles 5 with concentrated sulphuric acid and columns 4 with P_2O_5 . Next raise the temperature in the furnace to 800 °C, continuing to pass oxygen. Continue the heating for three hours. Collect the readily volatile UF_6 in ampoule 2 cooled by a mixture of acetone and dry ice (the temperature is about -70 °C). Seal the ampoule with the UF_6 on a soldering burner (in a fume cupboard!). Should the UF_6 be contaminated by hydrolysis products (upon insufficient drying of the oxygen), the product obtained must be distilled in a vacuum.

Experiment 11.7. PREPARATION OF UF_4 BY PRECIPITATION FROM AQUEOUS SOLUTIONS [5]

The reaction of U^{IV} with hydrofluoric acid or its salts leads to the formation of uranium tetrafluoride hydrates that are insoluble in water and in acid solutions:



Here the U^{VI} remains completely in the solution.

This method can be used to separate UF_4 from the fluorides of many metals because their solubility is much higher (except for the fluorides of thorium, zirconium, hafnium, the trivalent rare-earth elements, and the alkaline earth metals).

The U^{VI} can be reduced in the solution electrolytically or by the action of various reducing agents (rongalite, hydro-sulphite, sodium amalgam, tin chloride, etc.).

When UF_4 is precipitated within the temperature interval of 25-60 °C, the crystal hydrate $UF_4 \cdot 2.5H_2O$ is obtained, within the interval of 60-90 °C—the monohydrate, and at 100 °C—a hydrate of the composition $UF_4 \cdot \frac{3}{4} H_2O$.

Equipment and Reagents

Equipment. A platinum bowl. A platinum spatula. A water bath.

Radioactive Substances. UO_2SO_4 .

Reagents. $SnCl_2$, $Pb(CH_3COO)_2$, KNO_3 , K_2CO_3 . Solutions: 20% HF; NH_3 (not containing CO_2); 3% NH_4NO_3 ; 1 M NaOH; 10% NaCl; saturated $PbFCl$.

Performance of Work

Dissolve 6 g of UO_2SO_4 in 100 ml of water in the platinum bowl with heating on the water bath. Add to the solution a double amount (with respect to the calculated one needed

for reducing the U^{VI} of dry $SnCl_2$ and a double volume of a 20% solution of HF. Heat the reaction mixture during 30 min on the water bath with stirring. Filter off the precipitated heavy greenish blue hydrate of UF_4 with the aid of a paper filter without suction (preliminarily coat the funnel with a thin layer of paraffin). Wash the precipitate with water acidified with HCl up to the disappearance of the reaction for tin and dry it in a desiccator over P_2O_5 . Weigh the substance. Calculate the yield.

Analyse the preparation obtained for its content of U^{IV} and F.

Fuse together a weighed amount (~ 0.2 g) of the substance in the platinum bowl and 1 g of a mixture of KNO_3 and K_2CO_3 (1:4). Treat the melt with dilute HNO_3 (1:1) and precipitate uranium from the hot solution with ammonia. Next treat the precipitate in the same way as described in Experiment 11.3A.

Determine fluorine in the filtrate. Add a 1 M solution of NaOH up to a neutral reaction indicated by methyl red. Next add 10 ml of a 10% solution of NaCl and 3 ml of a solution of HCl (1:1) to the neutral solution. Introduce 5 g of CH_3COONa and 4 g of $(CH_3COO)_2Pb$ to the solution with heating. Heat the mixture on a water bath for two hours and let it stand overnight without filtering it. Filter off the finely crystalline precipitate on a sintered glass filter (No. 3), wash it with a saturated solution of $PbClF$, then with absolute ether, and dry it at $100^\circ C$.

Evaluate the content of crystallization water in the substance according to the difference between the masses of the dried and roasted precipitate.

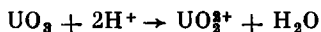
Determine the formula of the separated compound on the basis of the results of chemical analysis.

Experiment 11.8. PREPARATION OF SOLUBLE URANYL SALTS AND INVESTIGATION OF THEIR THERMAL STABILITY [16]

A feature of uranium(VI) is the formation of the uranyl ion UO_2^{2+} . All uranyl salts are yellow with a green fluorescence. Most of them crystallize well, are greatly hydrolyzed, and are readily soluble in water. The solutions have a clearly pronounced acid reaction. Uranyl salts heated in the air decompose with the formation of U_3O_8 as a product.

An important property of uranyl salts (especially its nitrate and sulphate) is their good solubility in certain organic solvents. This makes it possible to use the extraction method of purifying uranium from contaminants.

All the soluble uranyl salts can readily be prepared by dissolving UO_3 (obtained by roasting the peroxide hydrate at a temperature not exceeding 300°C) in acids:



Equipment and Reagents

Equipment and Utensils. A Kurnakov pyrometer. A continuous balance. A water bath. A porcelain bowl. A Büchner filter. A desiccator.

Radioactive Substances. UO_3 .

Reagents. Solutions: NH_3 containing no CO_2 ; 3% NH_4NO_3 ; 68% HNO_3 ; 96% H_2SO_4 ; 36% HCl ; 80% CH_3COOH .

Performance of Work

(a) Uranyl Nitrate

Gradually introduce 10 g of UO_3 into a solution of 6 ml of nitric acid (with a density of 1.4 g/cm^3) in 30 ml of water heated on the water bath. Filter the solution. Evaporate the filtrate on the water bath up to the appearance of a crystalline film, cool it to room temperature, suck off the precipitated crystals, and dry them on glass at room temperature.

(b) Uranyl Sulphate

Introduce 10 g of UO_3 in small portions into a solution of 2.5 ml of sulphuric acid (with a density of 1.84 g/cm^3) in 50 ml of water heated on the water bath. Filter the solution, evaporate the filtrate to the consistence of a syrup, cool it to room temperature, place it in the desiccator with concentrated sulphuric acid, and let it stand for several days. Suck off the crystals and dry them in the desiccator.

(c) Uranyl Chloride

Gradually introduce 10 g of UO_3 into a solution of 7 ml of hydrochloric acid (with a density of 1.19 g/cm^3) in 30 ml of water and heat it on the water bath up to complete dis-

solving. Filter the solution, and carefully evaporate the filtrate on the water bath (up to about two-thirds of the initial volume). Put the porcelain bowl with the solution in the vacuum desiccator with concentrated sulphuric acid and let it stand for a day. Separate the precipitate on a glass funnel with a filtering bottom closed with a ground glass cover. Dry the substance at a lowered pressure. Transfer the dry crystals into a tightly closing weighing bottle.

(d) Uranyl Acetate

Introduce 8.5 g of UO_3 into 50 ml of 80% acetic acid in small portions with heating on a water bath. Filter the solution, evaporate it on a water bath up to the formation of a crystalline film, cool it to room temperature, suck off the precipitated crystals, wash them with 3 ml of water, and dry them on glass at room temperature.

Evaporate the mother liquors remaining after separation of the crystals on the water bath. Precipitate ammonium diuranate with an NH_4OH solution while heating. Separate the precipitate, wash it with a 3% solution of NH_4NO_3 , dry it, and roast it to a constant mass at 800°C .

Determine the uranium content in the salts by the ammonia method (see Experiment 11.3A). Investigate the thermal stability, for which purpose register the heating curve on the Kurnakov pyrometer, and determine the change in the mass depending on the temperature of heating on the continuous balance. Use the data to determine the temperature conditions of decomposition, and also the composition of the products of decomposition of the separated salts.

Experiment 11.9. PREPARATION OF ANHYDROUS URANYL NITRATE [17]

Anhydrous uranyl nitrate cannot be prepared by simple dehydration of its hexahydrate because uranyl nitrate is a coordinationally unsaturated compound and loses its last molecules of water together with its decomposition.

The most suitable method is that of decomposing the unstable compound $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{NO}_2$ in a vacuum (165°C). This compound can be prepared either by the prolonged reaction of UO_3 with liquid NO_3 , or by precipitation from

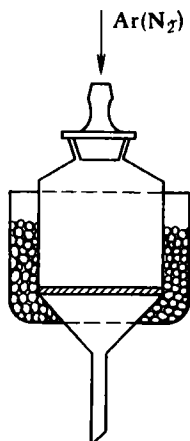


Fig. 11.5. Funnel with a filtering bottom for filtration in an inert atmosphere

a saturated solution of uranyl nitrate in TBP by fuming (containing 5-7% NO_3) nitric acid.

Anhydrous uranyl nitrate is a light yellow powder soluble in water. It readily adds molecules having electron donor properties. In the air, it rapidly transforms into a mixture of uranyl nitrate hydrates. It can absorb vapours of ether, acetone, alcohol, and nitrogen dioxide with the formation of complexes.

Equipment and Reagents

Equipment and Utensils. A vacuum installation. A water-jet pump. A funnel with a filtering bottom for filtration in an inert atmosphere (Fig. 11.5). A separatory funnel for 200 ml. Beakers for 200 ml (2). A test tube with ground-glass joint No. 19. A glass trap.

Radioactive Substances. $\text{UO}_2(\text{NO}_3)_2$.

Reagents. Tributylphosphate. Kerosene. Fuming nitric acid. 1,2-Dichloroethane. Liquid nitrogen. Nitrogen (in a gasometer).

Performance of Work

Prepare a saturated solution of uranyl hexahydrate in 100 ml of a 20% solution (by volume) of TBP in kerosene. Transfer the solution into the separatory funnel, shake it, and separate the organic phase from the aqueous one. Transfer the uranyl nitrate solution into a beaker and add 50 ml of

"fuming" nitric acid to it. Transfer the precipitated crystals together with the mother liquor onto a filter No. 2 for filtration in an inert atmosphere. Use the water-jet pump in an atmosphere of dry nitrogen (or argon) to separate the crystals from the solution, wash them with 1,2-dichloroethane, and dry on the filter in a stream of nitrogen.

Transfer the compound obtained into the Wurtz test tube with a ground-glass joint No. 19, and connect the tube via the trap cooled with liquid nitrogen to the vacuum installation. Heat the tube on an oil bath at 150-160 °C during two hours. After cooling the tube to room temperature, disconnect it from the vacuum line, and place the anhydrous uranyl nitrate into a weighed weighing bottle. Calculate the yield (in %). Store the substance in a paraffin-coated weighing bottle.

Experiment 11.10. PREPARATION OF SPARINGLY SOLUBLE URANYL SALTS [16]

The sparingly soluble salts of uranyl include trisubstituted phosphates, acid mono- and disubstituted double phosphates of uranyl and alkali metals, and also phosphates of uranyl and ammonium, the oxalate, uranylvanadates of alkali metals, molybdates, tungstates, and ferrocyanide. Some of the salts listed above [$\text{UO}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$, $(\text{UO}_2)_3(\text{PO}_4)_2$, $\text{UO}_2(\text{H}_2\text{PO}_4)_2$, UO_2HPO_4 , $(\text{UO}_2)_2\text{P}_2\text{O}_7$] are used in the technology for separating uranium.

Equipment and Reagents

Equipment and Utensils. A Kurnakov pyrometer. A continuous balance. An analytical balance. A press for preparing tablets. A water bath. A sintered glass filter. A chromatographic column filled with resin KU-2 in the H^+ form.

Radioactive Substances. $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{UO}_2(\text{CH}_3\text{COO})_2 \times \times 2\text{H}_2\text{O}$.

Reagents. Oxalic acid. Solutions: 0.1 M H_3PO_4 ; NH_3 (containing no CO_2); 3% NH_4NO_3 ; 0.5 M HCl; 4 M HCl.

Performance of Work

(a) Uranyl Oxalate

Dissolve a weighed portion of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (10 g) in 40 ml of water. Add 10 ml of a solution of $\text{H}_2\text{C}_2\text{O}_4$ saturated while heated on the water bath to the solution heated to

80-90 °C. Cool the solution with the precipitated crystals to room temperature, suck off the salt on a glass filter. Determine the pH of the mother liquor. Wash the substance on the filter with a solution of $\text{H}_2\text{C}_2\text{O}_4$ whose pH equals that of the mother liquor. Dry the preparation in the air.

Weigh the salt and calculate its yield.

Determine the uranium content in the substance, for which purpose roast an exactly weighed sample of the salt to a constant mass at 800 °C. Calculate the content of metallic uranium in the $\text{UO}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ in per cent according to the mass of the formed U_3O_8 .

To investigate the thermal stability of the compound, use the Kurnakov pyrometer to plot heating and cooling curves, and also a curve showing how the mass of the $\text{UO}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ changes when heated. Perform the experiment in the air and in an atmosphere of nitrogen thoroughly purified of oxygen. Use the results obtained to determine the temperature conditions of formation and the approximate composition of the products of uranyloxalate hydrate decomposition.

(b) Uranyl Orthophosphate

Dissolve a weighed portion of $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (5 g) in 65 ml of water. Slowly pour the solution with stirring into 70 ml of 0.1 *M* phosphoric acid. Filter off the precipitate. Wash the substance with a solution of CH_3COOH whose pH equals that of the mother liquor. Dry the salt at 50 °C.

Determine the uranium and phosphorus content in the preparation. For this purpose, separate these elements chromatographically on the resin KU-2 in the H^+ form. Dissolve a weighed sample (~ 0.2 g) of the salt in the minimum amount of 0.5 *N* HCl. Pass the resulting solution through the column with the resin (at a rate of 2 ml/min). Wash the resin with 200 ml of water. Combine the solution and the washing water. After preliminary evaporation, determine the phosphorus content in the solution of phosphoric acid by precipitating PO_4^{3-} in the form of NH_4MgPO_4 . Desorb the uranium by passing 100 ml of a 4 *M* solution of hydrochloric acid through the resin, and then washing the latter with 100 ml of water. Evaporate the solution and the washing water to a volume of 100 ml, then precipitate the uranium with a solution of NH_3 containing no CO_2 . Proceed with

the precipitate in the same way as described in Experiment 11.3A.

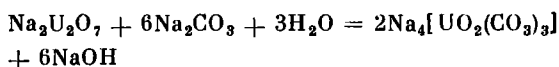
Determine the water content in the preparation with the aid of the continuous balance. Use the data of chemical and thermogravimetric analyses to determine the composition of the prepared salt.

Experiment 11.11. PREPARATION

OF URANATES [16]

Salts of uranic acid (uranates) can be prepared by roasting in the air a mixture of UO_3 or U_3O_8 with the relevant oxides or salts. Uranates also form upon the alkalization of aqueous solutions of uranyl salts, but here polyuranates are usually precipitated. Monouranates can be obtained only at high temperatures, the formation of monouranates of the alkali metals proceeding through the formation of diuranates.

Mono- and polyuranates are of a yellow or yellow-orange colour. All the uranates are insoluble in water, but dissolve well in acids with the formation of the uranyl ion or in carbonate solutions at the expense of the formation of a readily soluble complex compound. Sodium diuranate dissolves in sodium carbonate as follows:



Equipment and Reagents

Equipment and Utensils. A Kurnakov pyrometer. A continuous balance. An analytical balance. A press for preparing tablets. Platinum crucibles (2). Beakers for 200 ml (2) and for 100 ml (4).

Radioactive Substances. UO_3 . A 0.05 M solution of $\text{UO}_2(\text{NO}_3)_2$.

Reagents. Na_2CO_3 . K_2CO_3 . Solutions: 0.1 M NaOH; 0.1 M KOH; 20% pyridine; 3% NH_4NO_3 ; 5 M HNO_3 .

Performance of Work

(a) Preparation in Dry Way

Prepare 10 g each of mixtures of UO_3 with Na_2CO_3 and K_2CO_3 in the ratio of $\text{M}_2\text{O}:\text{UO}_3 = 1:1$.

Use weighed samples (~ 0.3 g) of the prepared mixtures for registering the change in the mass while heating on the

continuous balance. Plot the decrement of the mass against the temperature.

For each mixture preliminarily pressed into a tablet, register the heating curve on the Kurnakov pyrometer within the temperature range from 20 to 900 °C. After obtaining a series of converging thermograms for the reagents being studied, register the heating curves of the initial preparations (UO_3 , Na_2CO_3 , and K_2CO_3) in the same conditions for purposes of comparison.

Appraise the temperature of formation of the uranates, and also their composition on the basis of the data of thermal analysis.

Divide each of the remaining mixtures into two parts. Roast one in a platinum crucible up to a constant mass at a temperature corresponding to the formation of the diuranate, and the second at a temperature corresponding to the formation of the monouranate.

Study the individuality of the products by the X-ray method. Decipher the X-ray photographs in accordance with published data.

(b) Precipitation from Aqueous Solutions

Place 100 ml of an 0.05 *M* solution of $\text{UO}_2(\text{NO}_3)_2$ into each of the two 200-ml beakers. Heat the latter with their contents on the water bath. Slowly add a 0.1 *M* solution of NaOH with stirring to the hot solution in one of the beakers, and a 0.1 *M* solution of KOH to the other one, up to complete precipitation. Continue to heat the precipitates with the mother liquor during 12 hours. After complete coagulation and compacting of the precipitates, pour off the mother liquors, and wash the precipitate with hot water up to removal of the OH^- ions (the absence of a reaction to phenolphthalein). First dry the moist preparations in the air up to a constant mass, and then heat them in a drying cupboard at 135-140 °C, also up to a constant mass. Finally, roast them at 600 °C, and weigh the products again.

Determine the uranium content in the roasted products by the pyridine method. For this purpose, dissolve a weighed portion of the roasted product (~ 0.2 g) in nitric acid (1:1). Add a 20% solution of pyridine to the solution with stirring up to a neutral reaction (using methyl red), after which add another 10 ml of pyridine. Heat the solution, and if it again

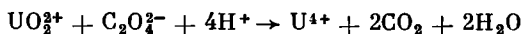
becomes acidic (according to the indicator), add more pyridine. Filter off the precipitate, wash it with a 3% solution of NH_4NO_3 containing a little pyridine, and roast it together with the filter up to a constant mass at 800-900 °C.

Use the results of chemical analysis to calculate the ratio $\text{M}_2\text{O} : \text{UO}_3$ in the roasted products. On the basis of the change in the mass when drying in the drying cupboard and roasting, appraise the content of water of crystallization in the air dry preparation and in the product obtained after holding in the cupboard at 135-140 °C.

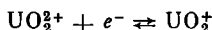
Compare the compositions of the preparations obtained in the dry way and by precipitation from a solution.

Experiment 11.12. PREPARATION OF URANIUM(IV) SULPHATE HYDRATES AND DETERMINATION OF THEIR COMPOSITION AND THERMAL STABILITY [18]

In sulphuric acid solutions in the presence of certain organic substances (ethanol, diethyl ether, oxalic acid, etc.) and under the action of light, UO_2^{2+} is reduced to U^{4+} . The photochemical reduction of U^{VI} to U^{IV} proceeds through the step of formation of unstable intermediate compounds of U^{V} . This is attended by decomposition (photolysis) of the organic substances*. The overall process of the photochemical reduction of uranium in the presence of oxalic acid goes on as follows:



It is possible to reduce UO_2^{2+} to U^{4+} electrochemically. This process is intricate and occurs through the formation of the ion UO_2^{2+} :

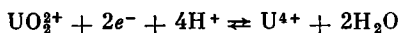


Hydrogen ions do not participate in the reaction because no formation or breaking of uranium-oxygen bonds is observed, and only the attachment of one electron occurs.

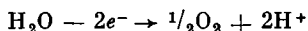
* To prepare uranium(IV) sulphate, such reducing agents as iron, aluminium, hydrosulphite, and sodium amalgam can be used. But the photochemical and electrochemical methods are the most convenient ones because in this case the uranium sulphate is not contaminated by foreign cations and requires no additional purification.

When an ion UO_2^+ transforms into an ion U^{4+} , the attachment of an electron is attended by breaking of a uranium-oxygen bond. The liberated oxygen reacts with hydrogen ions to form water molecules.

Hence, the overall process occurring on the cathode can be represented by the following equation:

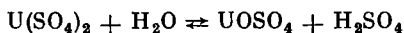


Oxygen is evolved in this process at the anode:



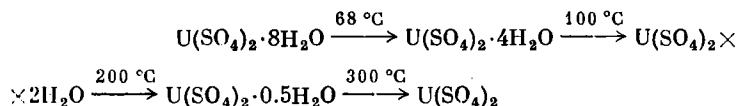
The sulphate U^{IV} is a green crystalline substance. It can be separated from aqueous solutions in the form of two crystal hydrates—the octahydrate $\text{U}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ and the tetrahydrate $\text{U}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$.

When dissolved in water, uranium sulphate is decomposed hydrolytically with the formation of the sparingly soluble basic sulphate of U^{IV} :



The presence of H^+ ions appreciably retards hydrolysis.

The concentration of the sulphuric acid solutions greatly affects the composition of the formed crystal hydrates. If it is 2-4%, the octahydrate is the reaction product, while an increase in the concentration to 5-8% leads to the formation of the tetrahydrate. In addition, in strongly acidic solutions, products may form that contain more than two sulphate ions per uranium atom. When heated, uranium sulphate hydrates lose their water in stages:



Heating in the air at a higher temperature leads to the formation of U_3O_8 .

Equipment and Reagents

Equipment and Utensils. A Kurnakov pyrometer. A continuous balance. An electrochemical cell. A mercury lamp. A beaker for 200 ml.

Radioactive Substances. $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$.

Reagents. Ethyl alcohol. Solutions: NH_3 containing no CO_2 ; 3% NH_4NO_3 ; concentrated H_2SO_4 .

Performance of Work

(a) Photochemical Reduction

Dissolve a weighed portion (5 g) of $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ in a mixture containing 20 ml of water, 12 ml of 96% alcohol, and 2.5 ml of concentrated sulphuric acid. Irradiate the solution with ultraviolet light during three or four hours. The reaction will be completed when the ion UO_2^{2+} is absent (test with potassium ferrocyanide).

Precipitate uranium sulphate by adding a surplus of alcohol to the dark green solution. Suck off the precipitate on a glass filter, wash off the excess sulphuric acid with a small amount of water at 0°C , and then with alcohol and ether (at room temperature). The dry preparation is stable in the air.

(b) Electrochemical Reduction

Use a mixture of a saturated solution of $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ with concentrated sulphuric acid as the electrolyte solution. For this purpose, dissolve 23 g of $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ in 100 ml of water, and add 6 ml of concentrated sulphuric acid. Put the solution into a glass electrolytic cell (Fig. 11.6) whose cathode is mercury layer 1 at the bottom of the vessel and whose anode is platinum plate 2 immersed in the electrolyte. Current is supplied to the cathode via platinum wire 4 soldered into a glass tube. Reduction proceeds quite rapidly at a current of 3-5 A. Transfer the precipitate formed during electrolysis back to the solution by adding a small amount of water. The reduction will be completed when the ion UO_2^{2+} is absent (test with potassium ferrocyanide).

By concentrating the solution in a vacuum over sulphuric acid or by evaporating it in the air at a temperature below 70°C , produce uranium sulphate hydrate. (The sulphate of U^{IV} can also be separated by precipitation with alcohol.)

Treat the precipitate in the same way as in photochemical reduction.

Appraise the composition of the obtained hydrates and also their thermal stability on the basis of the data of chemi-

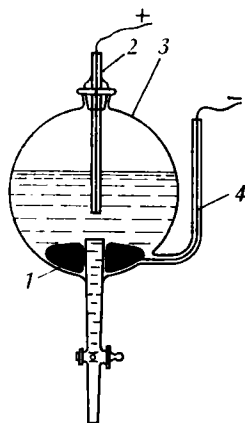
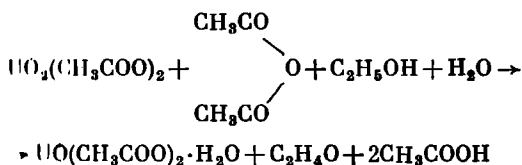


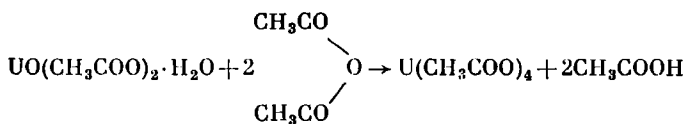
Fig. 11.6. Electrolytic cell for preparing uranium(IV) sulphate:
1—mercury cathode; 2—platinum anode; 3—vessel with electrolytic solution; 4—platinum wire

cal analysis (see Experiment 11.3A) and thermogravimetric investigation (recording of the curves in the Kurnakov pyrometer and on the continuous balance).

Experiment 11.13. PREPARATION OF URANIUM(IV) HYDROXYCARBOXYLATES AND CARBOXYLATES [19, 20]

The reduction of uranyl carboxylates (formate, acetate, propionate, etc., and also chloroacetates) by methyl alcohol under the action of ultraviolet light in the presence of the relevant anhydride (for formate—100% formic acid) leads to the formation of hydroxycarboxylates of U^{IV} that can be transformed into anhydrous carboxylates of U^{IV} by boiling with a surplus of the relevant anhydride in an atmosphere of CO_2 , for example for the acetate:





Like all salts of U^{IV} , the hydroxycarboxylates and carboxylates are coloured green.

Equipment and Reagents

Equipment and Utensils. A Kurnakov pyrometer. A continuous balance. An analytical balance. A tubular electric furnace (for 800°C). A Kipp gas generator for preparing CO_2 . A mercury lamp. A quartz tube 2-3 cm in diameter. A vacuum desiccator. A round-bottom flask for 500 ml with a reflux condenser. Wash bottles (2). A sintered glass filter.

Radioactive Substances. Uranyl carboxylates.

Reagents. Acetic anhydride (100% HCOOH , propionic anhydride, chloroacetic acids, etc.). Ethanol (95% and absolute). Concentrated H_2SO_4 .

Performance of Work

(a) Hydroxyacetate

Dissolve a weighed portion of $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (or another uranyl carboxylate (5 g) in 40-50 ml of water. Add 40 ml each of acetic anhydride and ethanol to the solution. Irradiate the mixture during two hours with ultraviolet light under the mercury lamp.

If the colour of the solution still retains a yellow tint, add 30 ml of alcohol, 30 ml of acetic anhydride, and irradiate with ultraviolet light for another hour. The solution will partly evaporate. After the appearance of the first crystals, place the solution in an ice bath. Separate the precipitate on a glass filter (No. 3), wash it on the filter with a small amount of absolute ethanol (3-5 ml), and dry in the vacuum desiccator over an alkali for 24 hours.

(b) Acetate of U^{IV}

Put a weighed sample (3 g) of the hydroxyacetate of U^{IV} (or another hydroxycarboxylate) into the 500-ml round-bottom flask with a reflux condenser and add 150 ml of acetic anhydride to it. The uranium hydroxyacetate, which is

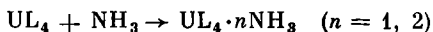
sparingly soluble in the acetic anhydride, forms a green suspension. Boil it for two hours with the simultaneous passing of CO_2 through it. Preliminarily dry the CO_2 and purify it of oxygen by consecutively passing it through the two wash bottles with concentrated sulphuric acid and over reduced copper heated to 600°C . Next cool the flask and pour its contents into a porcelain bowl. After the precipitate settles, decant the solution, transfer the precipitate onto the glass filter, wash it with absolute alcohol, and dry it in the vacuum desiccator over NaOH .

Determine the uranium content in the compounds by precipitation with ammonia (see Experiment 11.3A), and appraise the water content on the basis of the results of thermogravimetric analysis.

To investigate the thermal stability of the prepared salts, in addition to recording the heating curves on the continuous balance, plot heating curves by means of the Kurnakov pyrometer.

Experiment 11.14. PREPARATION OF AMMINES OF URANIUM(IV) CARBOXYLATES [20]

A specific feature of uranium as a complexing agent is the impossibility of obtaining ammonia complexes when treating its salts with aqueous ammonia solutions. In this case, either hydroxocomplexes or the hydroxide of U^{IV} form. Ammines of U^{IV} can be prepared by heterophase synthesis with the use of liquid or gaseous ammonia:



In such compounds, the nitrogen atom is coordinated directly to the uranium atom.

Ammines of uranium carboxylates have a gray-green colour, are hygroscopic, and oxidize in the air considerably more readily than the initial carboxylates. The relevant uranyl compound is the oxidation product. They decompose with the detachment of ammonia when heated to $80\text{--}120^\circ\text{C}$.

Equipment and Reagents

Equipment and Utensils. A vacuum installation. A glass trap. A Wurtz test tube with a ground glass joint No. 19 (2). A Dewar flask. A Wurtz flask for 500 ml (2). Drying columns (2). A vacuum desiccator. A magnetic stirrer.

Radioactive Substances. $\text{U}(\text{CHOO})_4$ or $\text{U}(\text{CH}_3\text{COO})_4$.

Reagents. A concentrated solution of NH_3 , granulated NaOH , dry ice, acetone, liquid nitrogen.

Performance of Work

Place 3 g of $\text{U}(\text{CHOO})_4$ into tube 1 (Fig. 11.7) connected via a ground glass joint to the vacuum installation. To remove the adsorbed water vapour, keep the substance under a vacuum for 20-30 min. Connect tube 2 cooled by a mixture of dry ice with acetone via the drying columns to the flask for preparing NH_3 . After 25-30 ml of liquid ammonia gather in the tube, disconnect it from the ammonia source and immerse about 0.5 g of cut up metallic sodium into the liquid ammonia. Connect tube 2 to the vacuum installation (see Fig. 11.7). Stopping the cooling of tube 2 and cooling tube 1 with liquid nitrogen, recondense the ammonia into the tube with uranium formate. Stir the mixture of solid $\text{U}(\text{CHOO})_4$ and NH_3 by means of the magnetic stirrer, then heat it to the melting point of ammonia (removing the cooling from the tube), after which again cool tube 1 with liquid nitrogen. Upon termination of the reaction, evacuate the surplus of ammonia, keeping the substance under the vacuum until a constant pressure sets in (~ 1.3 Pa).

Rapidly transfer the substance into a weighing bottle stored in the desiccator with a drying agent. Determine the uranium content in the compound by the method of "after-burning" (see Experiment 11.4).

Experiment 11.15. PREPARATION OF AMMONIUM TRICARBONATOURANYLATE [18]

The reaction of alkali metal or ammonium carbonates and bicarbonates with uranyl salts leads to the formation of complex ions of the type $[\text{UO}_2(\text{CO}_3)_3]^{4-}$, $[\text{UO}_2(\text{CO}_3)_2(\text{H}_2\text{O})_2]^{2-}$, etc. The most important in the technology of uranium production are the carbonate complex salts of sodium and ammonium.

Ammonium tricarbonatouranylate is a yellow crystalline substance soluble in water. Aqueous solutions are sufficiently

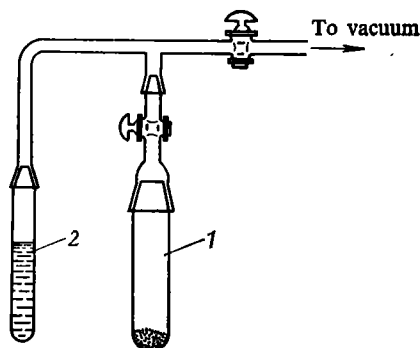
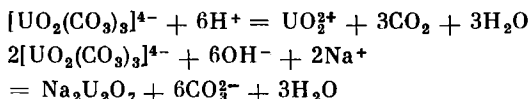


Fig. 11.7. Arrangement for preparing ammines of U^{IV} carboxylates:
 1—reaction tube cooled by liquid nitrogen; 2—tube for preparing liquid NH_3 cooled by a mixture of dry ice and acetone

stable, but acidification or alkalization causes decomposition of the complex anion:



When the dry salt is heated in the air up to 300-500 °C, it decomposes with the formation of UO_3 , NH_3 , CO_2 , and H_2O . Thermal dissociation without the access of air leads to the formation of UO_2 .

Equipment and Reagents

Equipment and Utensils. A Kurnakov pyrometer. A continuous balance. A water bath. A beaker for 200 ml. A funnel with a glass filtering bottom.

Radioactive Substances. $UO_2(NO_3)_2 \cdot 6H_2O$.

Reagents. A saturated solution of $(NH_4)_2CO_3$. Ethanol. Diethyl ether.

Performance of Work

Calculate the amount of $UO_2(NO_3)_2 \cdot 6H_2O$ needed for the preparation of 5 g of $[UO_2(CO_3)_3](NH_4)_4$. Dissolve the weighed amount of the initial salt at room temperature in a minimum volume of water and add with stirring a solution of $(NH_4)_2CO_3$ saturated at room temperature in an amount exceeding by

25% that needed for combining with the uranium into a complex compound. Heat the mixture on the water bath at 70 °C during 10-15 min. Let the solution with the precipitated crystals stand overnight, after which filter off the yellow crystals of ammonium tricarbonatouranylate with the aid of the glass funnel with a filtering bottom. Wash the crystals on the filter with small portions of 40-50% ethanol, then 2-3 times with 96% ethanol and 3-4 times with diethyl ether. Dry the crystals by sucking air through them.

Determine the uranium content in the complex by the ammonia method (see Experiment 11.3A).

Use the continuous balance and the Kurnakov pyrometer to study the thermal stability of the preparation. On the basis of the data obtained, determine the temperature conditions of formation and the composition of the products of decomposition of ammonium tricarbonatouranylate.

Experiment 11.16. PROCESSING OF TECHNICAL U_3O_8 [2, 5]

Work in a laboratory with uranium compounds is inevitably associated with the processing and purification of uranium residues. The roasting of many uranium compounds such as $UO_2(NO_3)_2 \cdot 6H_2O$, $UO_2C_2O_4 \cdot 3H_2O$, and $U(CH_3COO)_4$ in the air results in the formation of uranous-uranic oxide U_3O_8 . A number of compounds, however, for example uranates of the alkali, alkaline-earth and other metals except for ammonium diuranate, do not decompose when roasted. In addition, the decomposition products of uranium compounds often contain other substances besides U_3O_8 . The main task in processing U_3O_8 contaminated with impurities consists in separating pure uranium oxides containing no foreign elements.

Equipment and Reagents

Equipment and Utensils. A crucible furnace (for 600 °C). A drying cupboard. A porcelain bowl.

Radioactive Substances. U_3O_8 (or uranium residues to be regenerated).

Reagents. Solutions: HNO_3 (with density of 1.4 g/cm³); 10% $(NH_4)_2CO_3$; 25% NH_4OH ; 3% NH_4NO_3 .

Performance of Work

Calculate the amount of nitric acid (with a density of 1.4 g/cm^3) needed to dissolve 20 g of U_3O_8 . Put approximately twice this amount into the porcelain bowl. Introduce U_3O_8 (or uranium residues to be regenerated) into the acid in small portions with constant stirring. Add each following portion after the evolution of the brown NO_2 vapour (under a hood!) stops. Put the reaction mixture on a water bath. Evaporate it until almost dry for removal of the excess HNO_3 . Treat the residue with hot water. Filter the obtained solution through a fluted filter.

Test a small amount of the solution in a test tube for the presence of iron and certain other elements (Al, Co, Zn, Cd, etc.). To do this, add a 10% solution of $(\text{NH}_4)_2\text{CO}_3$ (10 ml) to the sampled solution with slight heating. Should a precipitate or turbidity appear in the tube, add a 10% solution of $(\text{NH}_4)_2\text{CO}_3$ to the entire filtrate in an amount (to be calculated) needed for combining the entire amount of uranium taken into a complex, and also a surplus in comparison with the calculated amount with a view to the presence of the impurities.

Filter off the precipitate. Decompose the complex by adding a solution of nitric acid (1:1) until the evolution of CO_2 terminates (with heating). Use NH_4OH to precipitate uranium from the solution in the form of ammonium diuranate. Separate the precipitate with the aid of a smooth filter, dry it in the drying cupboard, next transfer it into a crucible and roast at $350\text{--}400^\circ\text{C}$ in a crucible furnace.

For further purification, dissolve the trioxide in nitric acid so that 100 g of the nitric acid solution will contain 10 g of the uranyl nitrate. Add hydrogen peroxide following the procedure described in Experiment 11.4A to precipitate uranium peroxide hydrate, and after washing and drying the latter transform it into UO_3 at $350\text{--}400^\circ\text{C}$.

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Chapter 12 The Chemistry and Analysis of Thorium [1]

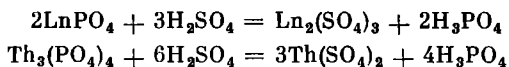
Experiment 12.1. SEPARATION OF THORIUM FROM MONAZITE [1-4]

Monazite is the most widespread thorium mineral. In the general form, its composition is expressed as follows: $(\text{Ce}, \text{La}, \text{Th}, \text{Ca})(\text{PO}_4, \text{SiO}_4, \text{SO}_4)$. Monazite is most often

represented, however, as a mixed phosphate of rare-earth elements and thorium. The content of thorium in it is usually 10-20%.

A. PROCESSING OF MONAZITE WITH SULPHURIC ACID

The method is based on the reaction of concentrated sulphuric acid with phosphates of the rare-earth elements and thorium:



(The symbol Ln is used here to signify all the lanthanides.)

When the sulphuric acid sinter is treated with water, phosphoric acid also passes into the solution together with the thorium and rare-earth element sulphates, and this greatly hampers the further processing of the solution. But this method is still used in practice.

Equipment and Reagents

Equipment and Utensils. A centrifuge. A mechanical stirrer. A sand bath or a Babo funnel. A Büchner filter. A porcelain bowl. Chemical beakers for 2 litres (2).

Radioactive Substances. Monazite sand.

Reagents. Solutions: saturated BaCl_2 ; concentrated H_2SO_4 .

Performance of Work

Thoroughly triturate a weighed portion (100 g) of monazite sand in a porcelain mortar and introduce it in small portions into the porcelain bowl with 150 ml of concentrated H_2SO_4 (preliminarily heat the sulphuric acid up to 200 °C on the sand bath or in the Babo funnel). Hold the suspension formed during four hours in the same conditions (200 °C), not letting the mass get heated to above 230 °C because at 230-250 °C thorium pyrophosphate forms, which is virtually insoluble in sulphuric acid solutions. A temperature below 200 °C is also undesirable because in these conditions the thorium concentrate settles to the bottom of the bowl forming a hard cake that is decomposed by the sulphuric acid only from the surface.

At the end of the decomposition, the substance is a dark gray paste. Cool it, and while mechanically stirring the solution, introduce the substance in small portions into a beaker

cooled with ice and containing about 600 ml of cold water. See that the temperature of the water in the beaker does not rise to above 20-25 °C, otherwise the leaching out will not be complete because the solubility of sulphates (especially those of the rare-earth elements) greatly decreases with elevation of the temperature. The same dependence of the solubility on the temperature also exists for thorium sulphate, but $\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$ and $\text{Th}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ readily form supersaturated solutions. This is why the losses of thorium due to a too high temperature of the solution in leaching out are usually smaller than the losses of the rare-earth elements.

Pour off the liquid from the solid residue and keep it. Repeat the leaching out, and combine the solutions. Dry the solid residue and again treat it with 50-80 ml of concentrated sulphuric acid in the conditions described above. Introduce the cooled mass with stirring into the ice-cooled extract from the first sulphuric acid treatment. After settling, filter off the cold liquid from the undissolved residue in a Büchner filter.

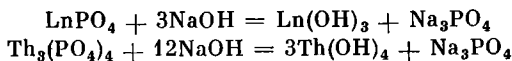
The transparent filtrate contains sulphates of thorium, rare-earth elements, and alkali metals, and also phosphoric acid and admixtures of salts of uranium, iron, aluminium, and other metals. The undissolved residue mainly consists of alkaline-earth metal sulphates and is discarded.

Add several millilitres of a saturated solution of BaCl_2 or $\text{Pb}(\text{CH}_3\text{COO})_2$ to the solution to remove the surplus of SO_4^{2-} ions from it. Separate the precipitate of barium or lead sulphate in a centrifuge or by filtration. The radium isotope mesothorium contained in the filtrate is removed with the barium sulphate.

The solution obtained in this way is used to separate thorium from the rare-earth and other accompanying elements (see Experiment 12.2).

B. ALKALINE PROCESSING OF MONAZITE

The method is based on the reactions:



The thorium and rare-earth element hydroxides obtained are filtered off from the sodium phosphate solution. Hence,

in the alkaline decomposition of monazite, the phosphate ions, which make processing of the mineral exceedingly complicated, are removed from the system already in the first stage of the process. The sodium triphosphate obtained is sufficiently pure and is used in practice. All this makes the alkaline method of processing more valuable than the acidic one, and the latter is giving way to a constantly growing extent to the alkaline method.

Equipment and Reagents

Equipment and Utensils. A sand or an air bath. A porcelain mortar. A chemical beaker for one litre.

Radioactive Substances. Monazite sand.

Reagents. Solutions: 45% NaOH; concentrated HNO_3 .

Performance of Work

Thoroughly triturate a weighed portion (100 g) of monazite sand in the porcelain mortar. Treat it with a double amount, in comparison with the theoretically calculated one, of a 45% solution of NaOH at 130-140 °C (the sand or air bath). Perform the process for two hours. Filter off the precipitate of hydroxides on a glass filter, wash it with water on the filter, and then dissolve it in a mineral acid. Use HCl or HNO_3 depending on the method employed later for separating the thorium from the rare-earth elements.

C. SEPARATION OF THORIUM FROM MONAZITES WHEN ANALYSING SILICATE ROCK

Monazite sand is decomposed by fusion with sodium peroxide; the thorium and rare-earth elements are precipitated in the form of oxalates. After decomposing the oxalates by heating with nitric acid, the thorium is determined photometrically with the aid of arsenazo I, quercetin, or 1-(pyridyl-2'-azo)-resorcinol.

Equipment and Reagents

Equipment and Utensils. A spectrophotometer. Porcelain crucibles No. 2 and 3. Chemical beakers for 100 and 250 ml. A measuring flask for 50 ml. Glass funnels (2).

Radioactive Substances. Monazite sand.

Reagents. Na_2O_2 . Solutions: 2 N HCl; 10 and 1% $\text{COOH}\cdot\text{COOH}$; HNO_3 (1 : 1). Arsenazo I.

Performance of Work

Place a weighed portion of monazite sand (50-100 mg) containing 250-500 μg of thorium into a porcelain crucible on whose bottom there is 0.5 g of sodium peroxide, and pour in 0.5 g more of sodium peroxide. Put the crucible into the other larger one and heat them on the flame of a burner, gradually raising the temperature up to the formation of a homogeneous melt.

Keep the molten mass in the liquid state about 10 min, cool it, and transfer it together with the crucible into a 100-ml beaker. Add 20-25 ml of water acidified with several drops of 2 *N* hydrochloric acid to the contents of the crucible in the beaker. Extract the crucible from the beaker, rinse it first with water, and then with 2 *N* hydrochloric acid; combine the washing water with the solution. Acidify the solution with 2 *N* hydrochloric acid to a pH of 1, introduce another 5 ml of the 2 *N* hydrochloric acid, and filter into another 250-ml beaker through small-pore size filter paper. Heat the filtrate up to the appearance of the first water vapour, add 10 ml of a hot 10% solution of oxalic acid, heat for another 1-2 min, and let the beaker stand overnight.

Filter off the thorium and rare-earth element oxalates on small-pore size filter paper, wash with a 1% solution of oxalic acid, and then wash off the precipitate with nitric acid (1 : 1) into a 100-ml beaker. Heat the solution up to the complete dissolving of the oxalates, evaporate it up to 5 ml, transfer it into a 50-ml measuring flask, bring the volume of the solution up to the mark by adding water, and stir it well. For analytical purposes, take an aliquot portion of the solution containing an amount of thorium ensuring the required accuracy in determination of its content by the selected photometric method.

Note. With a thorium content under 0.1%, decompose the monazite sand by treating the sample with sulphuric acid; at a thorium content above 0.5% increase the volume of the flask into which the solution of thorium and rare-earth elements is transferred, or decrease the aliquot portion in preparing the solution for photometric determination.

Experiment 12.2. SEPARATION OF THORIUM FROM RARE-EARTH ELEMENTS [1-3]

Thorium can be separated from the rare-earth elements accompanying it (in monazite and in most of the other thorium minerals) in various ways. Prior to the development

of the methods of extraction and ion-exchange separation of these mixtures, the main methods used were those of fractional precipitation of phosphates and hydroxides, and also methods based on the ability of thorium to form soluble carbonate and oxalate complexes.

A. FRACTIONAL PRECIPITATION OF THORIUM AND RARE-EARTH ELEMENTS IN THE FORM OF PHOSPHATES AND OXALATES

It is good practice to separate phosphates by fractional precipitation after the acid decomposition of the initial mineral when phosphoric acid is present in the solution in addition to thorium and rare-earth element sulphates. The same method is also applicable, however, in the alkaline method of processing monazite if the sodium phosphate formed upon decomposition is not filtered off. Here, when processing the reaction mixture with a mineral acid, chlorides (nitrates) of the rare-earth elements and thorium pass into the solution, and also phosphoric acid. In this case, there is no fundamental difference between the composition of the solutions obtained in acid or alkaline processing, and the method of fractional precipitation of phosphates is equally applicable.

Equipment and Reagents

Equipment and Utensils. A muffle furnace. A pH-meter with a glass electrode. A Büchner filter. Chemical beakers for 1 litre (2). Porcelain crucibles No. 3 (4).

Radioactive Substances. A solution containing salts of thorium, rare-earth elements, and PO_4^{3-} ions in a various degree of protonization (see Experiment 12.1) obtained in the sulphuric acid or alkaline decomposition of monazite sand.

Reagents. Solutions: 25% NH_4OH ; concentrated HCl ; saturated oxalic acid; 25% Na_2CO_3 or $(\text{NH}_4)_2\text{CO}_3$; saturated $(\text{NH}_4)_2\text{C}_2\text{O}_4$; 1 *M* $\text{Na}_2\text{S}_2\text{O}_3$.

Performance of Work

Heat an acid solution containing salts of thorium, rare-earth elements, and phosphoric acid in a chemical beaker up to boiling and carefully neutralize with ammonia or magnesium oxide to a pH of 1.1 (control the pH with the aid of the pH-meter). Thorium pyrophosphate precipitates:



Filter off the precipitate in the Büchner filter and increase the pH of the filtrate to 2.3. Filter off the rare-earth element phosphates that precipitate. Neutralize the filtrate to a pH of 6-8. The residues of the rare-earth elements and thorium precipitate. Roast the precipitate in a porcelain crucible and combine it with a new portion of monazite sand to be decomposed.

To obtain thorium and rare-earth element preparations as pure as possible in the fractional precipitation of the phosphates, neutralize the solutions very carefully and stir them well, not permitting a local surplus of the alkali.

Note. The best results are obtained in separating thorium and the rare-earth elements if "homogeneous" precipitants are used such as hexamine $(\text{CH}_2)_6\text{N}$ and urea $(\text{NH}_2)_2\text{CO}$. These reagents are soluble in water, they gradually hydrolyze when the solution is boiled, and the pH of the solution increases uniformly throughout the entire volume of the solution.

As a result of neutralization with ammonia, 98-99% of the thorium transforms into the pyrophosphate; the admixture of rare-earth elements in this precipitate is 5-7%.

It is convenient to purify the phosphates of thorium and the rare-earth elements by the oxalate-carbonate method. For this purpose, dissolve the precipitates of the thorium and rare-earth element phosphates, each separately, in a minimum amount of concentrated hydrochloric acid. Heat the solutions to 60 °C and add a surplus of a saturated solution of oxalic acid. Filter off the formed precipitate of oxalates; the solution contains well soluble complex oxalates of iron, aluminium, and uranium. First wash the precipitates on the Büchner filter with dilute solutions of oxalic and a mineral (H_2SO_4 , HNO_3 , HCl) acids to remove the coprecipitated phosphates and the adsorbed H_3PO_4 , and then with water. Add about one litre of a 25% solution of Na_2CO_3 or $(\text{NH}_4)_2\text{CO}_3$ to each of the moist precipitates of thorium oxalate and the rare-earth element oxalates. Boil the mixtures. The thorium passes into the solution because of the formation of a soluble pentacarbonate complex $\text{Na}_6[\text{Th}(\text{CO}_3)_5]$ or $(\text{NH}_4)_6[\text{Th}(\text{CO}_3)_5]$. The oxalates of the rare-earth elements transform into insoluble double carbonates and remain in the precipitate. Their composition is $\text{Ln}_2(\text{CO}_3)_3 \cdot \text{Me}_2\text{CO}_3 \cdot 12\text{H}_2\text{O}$.

The method of carbonate purification gives good results if thorium, which passes into the solution in a sufficiently

pure state, predominates in the mixture being separated. Conversely, it is more convenient to purify the oxalate precipitate obtained from phosphates containing mainly rare-earth elements from an admixture of thorium by treatment with a surplus of ammonium oxalate. The thorium forms the soluble complex $(\text{NH}_4)_4[\text{Th}(\text{C}_2\text{O}_4)_4]$, while the rare-earth elements, especially of the cerium subgroup, remain in the precipitate. Wash the basic carbonates of the rare-earth elements filtered off from the solution of the thorium carbonate complex with a soda solution and dissolve them in hydrochloric acid. Precipitate the rare-earth elements from the solution obtained in the form of oxalates and then roast them at 900°C to oxides. [The purity of the rare-earth element oxides, and also of the thorium preparations, can be appraised photometrically (see Experiment 12.3D).]

Acidify the thorium pentacarbonate solution with a mineral acid up to the appearance of a precipitate of the basic carbonate $\text{Th}(\text{OH})_2\text{CO}_3 \cdot 8\text{H}_2\text{O}$.

Use $\text{Na}_2\text{S}_2\text{O}_3$ for final purification of the thorium preparation. For this purpose, dissolve the basic thorium carbonate in a minimum amount of concentrated hydrochloric acid, evaporate the solution until dry, dissolve the thorium chloride in water and precipitate the thorium at 60°C with a solution of $\text{Na}_2\text{S}_2\text{O}_3$. Filter off the precipitate, dry it, and roast it at 800°C to ThO_2 .

B. SEPARATION OF THORIUM FROM RARE-EARTH ELEMENTS BY THE EXTRACTION METHOD

Equipment and Reagents

Equipment and Utensils. A muffle furnace for 900°C . A separatory funnel. A Büchner filter. Porcelain crucibles No. 3 (3). Beakers for one litre (2) and for 500 ml (2).

Reagents. Oxalic acid. NaF. Solutions: 4 M HNO_3 . 30% H_2O_2 ; 40% tributylphosphate (TBP) in xylene, kerosene, or dibutyl ether.

Performance of Work

Separate mixtures of thorium and rare-earth metals by the method of extraction with TBP, using aqueous solutions of thorium and rare-earth metal nitrates. To prepare a solution of the relevant nitrates, process the precipitate of

thorium and rare-earth element hydroxides obtained in the alkaline breakdown of monazite with nitric acid.

After sulphuric acid decomposition of monazite, proceed as follows. Treat the solution of thorium and rare-earth metal sulphates freed of its surplus of SO_4^{2-} ions* with a saturated solution of oxalic acid up to complete precipitation.

Filter the precipitate of rare-earth element and thorium oxalates in a Büchner filter and wash it on the filter with dilute nitric acid, and then with water. Next dry the precipitate, place it into porcelain crucibles, and roast it up to the formation of oxides in the muffle furnace at 900°C .

Treat the oxides of the rare-earth elements and thorium while heating with concentrated nitric acid. If they dissolve slowly, add a little (on the tip of a scalpel!) NaF or NH_4F .

The solution of nitrates is coloured red-orange owing to the presence of $\text{Ce}(\text{NO}_3)_4$. Since $\text{Ce}(\text{NO}_3)_4$ and $\text{Th}(\text{NO}_3)_4$ have similar extraction properties, preliminarily reduce the Ce^{4+} with hydrogen peroxide to Ce^{3+} (the red colour should disappear completely).

Separate the nitrate of Th^{IV} from the nitrates of the rare-earth elements(III) by shaking the nitrate aqueous solution with a 40% solution of TBP in an inert organic solvent, for example in xylene (the organic solvent is added to lower the density of the organic phase, which is required for rapid separation of the phases in extraction).

The solution of nitrates must be 4 M with respect to HNO_3 . For the concentration of the HNO_3 not to lower in the course of extraction, preliminarily saturate the organic phase with HNO_3 , shaking the solution of TBP several times in the separatory funnel with new portions of 4 M HNO_3 . Calculate the amount of TBP assuming that the compound $\text{Th}(\text{NO}_3)_4 \cdot 2\text{TBP}$ forms in the organic phase. The density of the TBP is 0.973 g/ml. Hence, 100 ml of a 40% solution of TBP in xylene contains $(0.973 \text{ g/ml} \times 40 \text{ ml}) = 39 \text{ g}$ of TBP, i.e. 0.325 mol of TBP. Consequently, 100 ml of such a solution can extract 0.08 (i.e. $0.325/4$) mol of thorium nitrate from the aqueous phase into the organic one in the form of $\text{Th}(\text{NO}_3)_4 \cdot 2\text{TBP}$, which when converted to ThO_2 forms 18 g.

* If the solution contains a surplus of a mineral acid, neutralize it before the oxalate precipitation to a pH of 3 or 4 by adding NH_4OH or Na_2CO_3 .

After separation of the phases, separate the organic phase from the aqueous one, and to remove the impurities of the trivalent rare-earth elements, wash it twice with water, and then reextract the thorium nitrate with 0.02 *N* nitric acid.

Treat the nitric acid aqueous solutions of the nitrates of the rare-earth elements and thorium obtained as a result of extraction separation in accordance with how the purified preparations are to be used subsequently. For example, the corresponding hydroxides can be separated by acting with NH_4OH , or oxalates by acting with oxalic acid. Roast the hydroxides or oxalates at 800 °C to obtain oxides of the rare-earth elements and thorium oxide convenient for storage and for further use. (For the analysis of the obtained preparations, see Experiment 12.3.)

C. CHROMATOGRAPHIC SEPARATION OF THORIUM FROM ITS ACCOMPANYING ELEMENTS *

Sorb the ions of thorium and the accompanying elements with the strongly basic cation exchanger KU-2 in the H^+ form. Next desorb the titanium admixture with 1 *N* hydrochloric acid, rare-earth elements with 2 *N* hydrochloric acid, zirconium with a 0.5% solution of oxalic acid, and thorium with a saturated solution of ammonium oxalate. Determine the thorium in the filtrate by photometric or complexometric techniques depending on its amount.

The method can be used to determine the presence of 10^{-3} - $10^{-4}\%$ of thorium in any silicate rock containing large amounts of zirconium, titanium, and rare-earth elements.

Equipment and Reagents

Equipment and Utensils. A Pulfrich photometer or a photocolormeter. A chromatographic column (diameter 0.5 cm, height 30 cm) filled with the cation exchanger KU-2 in the H^+ form (grain size 50-100 mesh) to a height of 24-25 cm. A sand bath. A nickel crucible. Beakers for 250 and 100 ml. A funnel.

Radioactive Substances. Silicate rock containing thorium.

Reagents. Sodium peroxide. Solutions: dilute (1:1), 1 and 2 *N* HCl; 25% and 1 *M* NH_4OH ; 0.1 *M* oxalic acid; saturated $(\text{NH}_4)_2\text{C}_2\text{O}_4$ (density 1.4 g/cm³).

* Use this procedure only when analysing silicate rock.

Performance of Work

Fuse a weighed portion (0.1-0.2 g) of thoroughly triturated silicate rock in the nickel crucible with 4-5 g of Na_2O_2 until a homogeneous melt is obtained. After cooling the crucible, place it in a 250-ml beaker and add 100 ml of water. Cover the beaker with a watch glass and heat it for 15-20 min on a sand bath. Extract the crucible from the beaker with a glass rod, rinse it with water, and combine this water with the main solution.

Filter the precipitate on medium-size pore filter paper, dissolve it in 30-40 ml of hydrochloric acid (1:1), and dilute the solution with water, bringing its volume up to 100 ml. Add 25% NH_4OH to the solution with stirring until a strong odour appears, filter the precipitate on medium-size pore filter paper, wash it five or six times with 1 *M* NH_4OH , and dissolve it on the same filter with 20-25 ml of hot 1 *N* HCl .

Cool the solution and pass it at a rate of 5-6 drops a minute through the chromatographic column 0.5 cm in diameter and 30 cm high filled to a height of 24-25 cm with the cation exchanger KU-2 in the H^+ form. Wash the resin with 20 ml of 2 *N* HCl and 7 ml of 0.1 *M* $(\text{NH}_4)_2\text{C}_2\text{O}_4$, and discard the solution flowing out of the column.

Next pass 20 ml of a saturated solution of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ through the column, gather the filtrate into a 100-ml beaker, evaporate it until dry on the sand bath, add 5 ml of nitric acid (with a density of 1.4 g/cm^3), and evaporate to a volume of 1-2 ml. Determine thorium in the obtained solution by any photometric method*.

Experiment 12.3. QUANTITATIVE DETERMINATION OF THORIUM

A. IODATE METHOD WITH IODOMETRIC TERMINATION [5, 6]

The method consists in precipitating thorium ions with a solution of KIO_3 , washing the thorium iodate precipitate with a nitric acid solution of KIO_3 , dissolving the precipitate

* When determining thorium by the photometric method with the aid of arsenazo III, evaporation of the thorium oxalate with HNO_3 is not obligatory because the oxalate ions are not a hindrance.

in H_2SO_4 with the addition of KI, and titration of the evolved iodine with a solution of $\text{Na}_2\text{S}_2\text{O}_3$ in the presence of starch. To obtain a precipitate corresponding to the formula $4\text{Th}(\text{IO}_3)_4 \cdot \text{KIO}_3 \cdot 18\text{H}_2\text{O}$, one must strictly adhere to the conditions indicated in the precipitation procedure. The determination is hindered by zirconium, titanium, uranium(IV), and cerium(IV). The titanium and zirconium can be masked by adding oxalic acid, the uranium(IV) is oxidized to the uranyl ion, and the cerium is reduced with hydrogen peroxide.

The method makes it possible to determine 4-16 mg of thorium in the presence of Ce^{III} and rare-earth elements with an error not exceeding 3-4%.

Equipment and Reagents

Utensils. A beaker for 50-100 ml. A funnel. A measuring flask for 100 ml. A pipette for 20 ml. A conical flask for 300 ml.

Radioactive Substances. A solution containing 4-16 mg of Th in 10 ml.

Reagents. Methyl alcohol. Solutions: 15% KIO_3 in 50% HNO_3 (by volume); 1% KIO_3 in HNO_3 (1:9); HNO_3 (density 1.4 g/cm³); H_2SO_4 (1:1); 5% KI; 1% starch; 0.05 M $\text{Na}_2\text{S}_2\text{O}_3$.

Performance of Work

Add 5 ml of nitric acid (with a density of 1.4 g/cm³) to 10 ml of a solution containing 4-16 mg of Th, introduce 10 ml of a 15% solution of KIO_3 in dilute (1 : 1) nitric acid, and let the mixture stand during 0.5 or 1 hour, stirring from time to time, up to complete coagulation of the precipitate. Filter the latter off on small-size pore filter paper, wash it off the walls of the beaker with a 1% solution of KIO_3 in dilute (1 : 9) nitric acid, and wash with methyl alcohol up to a negative reaction for the IO_3^- ion (test with KI in H_2SO_4). Next transfer the filter with the precipitate into the beaker in which precipitation was performed, add 10 ml of dilute (1 : 1) sulphuric acid, and after complete dissolving of the precipitate, filter the solution into the 100-ml measuring flask, dilute it with water bringing the volume up to the mark, and stir well.

Transfer an aliquot part of the solution (20 ml) with the pipette into the 300-ml conical flask, add 20 ml of a 5% solution of KI, let the mixture stand in a dark spot for

5 min, add 100-150 ml of water, and titrate with a 0.05 *M* solution of $\text{Na}_2\text{S}_2\text{O}_3$ up to the appearance of a straw yellow colour. After this introduce 1-2 ml of a 1% solution of starch and continue to titrate with the $\text{Na}_2\text{S}_2\text{O}_3$ solution up to complete decolouration of the solution being titrated from one drop of the thiosulphate solution. Perform the titration up to the obtaining of three converging results. 1 ml of an 0.05 *M* solution of $\text{Na}_2\text{S}_2\text{O}_3$ is equivalent to 0.114 mg of Th.

B. IODATE-COMPLEXONOMETRIC METHOD OF DETERMINING THORIUM [7]

The method consists in separating thorium from the accompanying elements in the form of the iodate, dissolving the filtered off precipitate in a definite amount of a standard solution of Na-EDTA, and titrating off the surplus of the Na-EDTA with a standard solution of CuSO_4 in the presence of 1-(2'-pyridylazo)-2-naphthol as an indicator. At the final point of titration, the greenish colour of the solution sharply changes to a red-violet one from one surplus drop of the CuSO_4 solution. The thorium iodate precipitate may have any composition, and there is no need to remove the surplus of the precipitant as in the previously proposed procedures. By performing precipitation in the presence of oxalic acid, the thorium can be separated from Ti, Zr, Ce^{IV} , and U^{IV} , which are precipitated by an iodate in an acid medium.

The error in determining 4-20 mg of Th does not exceed 3-4%.

Equipment and Reagents

Equipment and Utensils. A sand bath. A conical flask for 100 ml. A beaker for 100 ml.

Radioactive Substances. A solution containing 4-20 mg of Th.

Reagents. Solutions: HNO_3 (density 1.4 g/cm³); 15% KIO_3 in HNO_3 (1:1); 0.5% KIO_3 in 1 *N* HNO_3 ; 0.01 *M* Na-EDTA; 0.01 *M* CuSO_4 ; 0.1% 1-(pyridyl-2'-azo)-2-naphthol in methanol; 1 *M* NH_4OH .

Performance of Work

To a solution with a volume of 10 ml containing 4-20 mg of Th add 6-7 ml of a solution of HNO_3 (density 1.4 g/cm³), dilute with water up to 25 ml, add 5 ml of a 15% solution of KIO_3 in dilute (1 : 1) nitric acid, and heat on the sand bath

up to complete coagulation of the precipitate. Filter off the precipitate on small-size pore filter paper, wash three or four times with a 0.5% solution of KIO_3 in 1 *N* nitric acid, transfer together with the filter into the beaker in which precipitation was performed, introduce 15 ml of a 0.01 *M* solution of Na-EDTA, neutralize with a 1 *N* solution of NH_4OH to a pH of 3-4 according to universal indicator paper, and heat on the sand bath up to complete dissolving of the precipitate (10-15 min at 80-90 °C). Filter off the paper flakes, wash them several times with water, gather the filtrate and the washing water in the 100-ml conical flask, add 3-4 drops of a 0.1% solution of 1-(pyridyl-2'-azo)-2-naphthol in alcohol, and titrate the surplus of Na-EDTA with a 0.01 *M* solution of CuSO_4 until the yellow-green colour of the solution changes to a red-violet one (1 ml of a 0.01 *M* solution of Na-EDTA is equivalent to 2.32 mg of Th)*.

C. COMPLEXONOMETRIC TITRATION OF THORIUM
IN THE PRESENCE OF
1-(PYRIDYL-2'-AZO)-2-NAPHTHOL [8]

Thorium(IV) forms with Na-EDTA a complex compound in the molar ratio 1 : 1 that is stable in an acid medium (the instability constant is $10^{-23.2}$). Complexonometric titration can be performed already at a pH of 1.8, when many other ions still do not form stable complexonates.

Several indicators have been proposed for detecting the end point of titration. The most selective of them is 1-(pyridyl-2'-azo)-2-naphthol allowing titration to be performed within the pH interval of 2.0-3.5. A solution of a thorium salt in the presence of 1-(pyridyl-2'-azo)-2-naphthol has an orange-red colour. When Na-EDTA is added, the solution's colour changes through yellow-orange to greenish yellow. The transition of the orange-red colour to yellow-green occurs when about half of the thorium has been titrated; upon further titration, the yellow-orange colour continues to change slowly. A clear transition to greenish yellow occurs

* During titration, it is necessary to keep the pH of the solution being titrated not lower than 3, otherwise it will acquire a red-violet colour when the very first drop of CuSO_4 is added because at $\text{pH} < 3$ the compound of copper with 1-(pyridyl-2'-azo)-2-naphthol is more stable in comparison with the copper complexonate.

from one surplus drop of the Na-EDTA solution and corresponds to the end point of titration.

The determination of Th^{IV} is not hindered by large amounts of ions of the alkali and alkaline-earth metals, U^{IV} and U^{VI} , La^{III} , Ce^{III} , traces of Ce^{IV} , Sr^{II} , and Pb^{II} , and large amounts of SO_4^{2-} . It is hindered by Ni^{II} , Bi^{III} , In^{III} , and V^{V} which form coloured compounds with 1-(pyridyl-2'-azo)-2-naphthol that are stable in an acid medium, and by F^- , PO_4^{3-} , $\text{C}_2\text{O}_4^{2-}$, and other ions forming precipitates or complex compounds with Th^{IV} ; Zn^{II} , Cd^{II} , Mn^{II} , Cr^{III} (2.5 mg/ml) and Cr^{VI} (0.6 mg/ml) change the tint of the solution being titrated, but the transition to the end point can be seen quite clearly. In the presence of Hg and Sn^{II} , the solution becomes turbid toward the end of titration, which hinders the establishment of the end point; Ti^{IV} and Zr^{IV} hydrolyze, adsorbing the indicator, and also hinder the determination of Th^{IV} . In the presence of Al^{III} , titration is performed at a pH of 2.5; Fe^{III} is preliminarily reduced with the aid of ascorbic acid.

The method makes it possible to determine Th^{IV} in monazite sands and thorium-containing materials after the separation of phosphates.

When titrating Th^{IV} in pure solutions, the system Cu^{II} complexonate and 1-(pyridyl-2'-azo)-2-naphthol may be used as the indicator and titration performed at a pH of 3-4. When Cu^{II} complexonate is added to a solution containing Th^{IV} , the more stable Th^{IV} complexonate is formed, while the Cu^{II} yields with the 1-(pyridyl-2'-azo)-2-naphthol a red-violet compound that is decomposed by Na-EDTA. When Na-EDTA is introduced into the solution, first the complexonate Th^{IV} forms, and then the complexonate Cu^{II} . The colour of the solution sharply changes from red-violet to yellow-green from one surplus drop of the Na-EDTA solution. For a still sharper change in the colour, the solution is heated to 70-80 °C prior to titration.

Equipment and Reagents

Equipment and Utensils. A measuring flask for 50 ml. A pipette for 15 ml. A conical flask for 100 ml.

Radioactive Substances. A solution containing 50-100 mg of Th.

Reagents. Solutions: 0.01 M Na-EDTA; 1 M NH_4OH ; 1 N HCl; 1 M $\text{NH}_4\text{CH}_3\text{COO}$; 0.1% 1-(pyridyl-2'-azo)-2-naphthol in methanol (or ethanol); 0.01 M of Cu^{II} complexonate.

Performance of Work

Dilute a solution containing 50-100 mg of Th with water acidified with 1 *N* hydrochloric acid (1 ml) in the 50-ml measuring flask, bringing the volume up to the mark. Transfer 15 ml of the prepared solution with the pipette into the 100-ml conical flask, introduce 3-5 drops of a 0.1% solution of 1-(pyridyl-2'-azo)-2-naphthol and add several drops of 1 *M* NH_4OH up to the appearance of an orange-red colour. Titrate the solution with a 0.01 *M* solution of Na-EDTA until the orange-red colour of the solution changes into a greenish yellow one (1 ml of a 0.01 *M* solution of Na-EDTA is equivalent to 2.32 mg of thorium).

When foreign ions are present, add 3-5 drops of the solution of 1-(pyridyl-2'-azo)-2-naphthol to the solution containing Th^{IV} . If a pink or red colour appears, add one or two drops of 1 *N* hydrochloric acid up to the appearance of an orange colour, and titrate with a 0.01 *M* solution of Na-EDTA.

When titrating in the presence of the indicator system including Cu^{II} complexonate and 1-(pyridyl-2'-azo)-2-naphthol, add 3-5 drops of a 0.01 *M* solution of Cu^{II} complexonate and 3-5 drops of a 0.1% alcohol solution of 1-(pyridyl-2'-azo)-2-naphthol to an aliquot part of the solution being analysed containing 15-30 mg of Th^{IV} (15 ml from the 50-ml measuring flask), dilute with water to a volume of 25-30 ml, introduce 1-2 ml of a 1 *M* solution of $\text{NH}_4\text{CH}_3\text{COO}$ up to a pH of 3 or 4 according to universal indicator paper, heat to 70-80 °C (the appearance of water vapour), and titrate with a 0.01 *M* solution of Na-EDTA until the red-violet colour of the solution changes to a yellow-green one from one drop of the solution of Na-EDTA.

D. PHOTOMETRIC DETERMINATION OF THORIUM WITH QUERCETIN [3, 9]

Quercetin (3,5,7,3',4'-pentahydroxyflavone) is employed for the photometric determination of various elements, including Th^{IV} ($\lambda_{\text{max}} = 425 \text{ nm}$), Be^{II} ($\lambda_{\text{max}} = 400 \text{ nm}$), Ga^{III} ($\lambda_{\text{max}} = 437 \text{ nm}$), In^{III} ($\lambda_{\text{max}} = 425 \text{ nm}$), Zr ($\lambda_{\text{max}} = 450 \text{ nm}$), and UO_2^{2+} ($\lambda_{\text{max}} = 455 \text{ nm}$).

In an alcohol-water medium, quercetin forms a yellow compound with the Th^{IV} ion that can be used for photometric determination.

Solutions of the reagent have two peaks of light absorption: at 255 nm and 365 nm; solutions of the compound of quercetin with Th^{IV} have their maximum absorption at 440 nm, but it is better to measure the optical density at 455 nm, at which the light absorption of the reagent is insignificant. Coloured solutions of the compound of thorium with quercetin are stable for 20-30 h at an ethanol concentration of 40% (by volume). The stability grows with an increase in the concentration of the alcohol. The Bouguer-Lambert-Beer law is observed within the concentration interval from 1 to 10 $\mu\text{g}/\text{ml}$ of Th. The optimal value of the solution's pH is 3.4-6.5, but to avoid hydrolysis it is better to use a pH of 3.4-4.0 (an acetate-ammonia buffer solution).

The determination is not hindered by ions of the rare-earth elements, consequently this method can be used when analysing monazite sand after the separation (in the form of oxalates) of thorium together with all the rare-earth elements.

Equipment and Reagents

Equipment and Utensils. A Pulfrich photometer. Measuring flasks for 250 ml (6). A burette for 25 ml.

Radioactive Substances. A solution of $\text{Th}(\text{NO}_3)_4$ containing 25 $\mu\text{g}/\text{ml}$ of Th.

Reagents. Methanol (or ethanol) or acetone. Solutions: 0.05% quercetin in methanol (ethanol) or acetone; acetate-ammonia buffer with pH = 3.4-4.0 (mix 102 ml of glacial CH_3COOH with 22 ml of 25% NH_4OH and dilute with water up to two litres).

Performance of Work

To each of five 25-ml measuring flasks containing 15 ml of alcohol (or acetone) add 2 ml of a 0.05% solution of quercetin, then 1, 2, 3, 4, and 5 ml (respectively) of a solution of $\text{Th}(\text{NO}_3)_4$ containing 25 $\mu\text{g}/\text{ml}$ of Th, and gradually, with constant stirring, 5 ml of the buffer solution (when this solution is added rapidly, the thorium may hydrolyze and form no coloured compound). In 20 min, dilute the solutions up to the mark with water, and measure their optical density with respect to water in a universal photometer with the corresponding light filter. Plot a calibration graph.

In a similar way, analyse the solution with an unknown amount of Th, which is determined according to the calibration graph.

E. PHOTOMETRIC DETERMINATION OF THORIUM WITH ARSENAZO I [40]

The photometric determination of Th^{IV} with the aid of arsenazo I is based on measuring the optical density of solutions of their compounds. Pink solutions of arsenazo I form a blue-violet complex compound with Th^{IV} ions in a weakly acidic medium. The peak of light absorption of the solutions is at 580 nm. The optimal pH is 1.3-3.0. The compound forms immediately when the solutions of the components are poured together and does not change when held in dispersed light for a month. The Th^{IV} ions react with the arsenazo I in a molar ratio of 1 : 1 (established by the method of isomolar series); the instability constant is 1.6×10^{-16} . The sensitivity of the method is 0.7 $\mu\text{g/ml}$ of Th. The maximum development of the colour is observed when 2-3 mg of arsenazo I are contained in 50 ml of the solution.

In the conditions of the determination, the ions U^{IV} , Pu^{IV} , Ti^{IV} , Zr^{IV} , Fe^{III} , and Al^{III} react with arsenazo I to form compounds with a violet colour of various tints. Rare-earth elements do not hinder the determination at a pH of 1.9 even when their predomination is 1300-fold. This makes it possible to separate thorium from the hindering ions in the form of the oxalate, using the rare-earth elements as carriers. Among anions, F^- , SO_4^{2-} , PO_4^{3-} , and others forming precipitates or complex compounds with Th^{IV} are a hindrance.

The determination of Th^{IV} with arsenazo I can be performed without separating Zr^{IV} and Ti^{IV} by introducing tartaric acid (for masking the zirconium) and ascorbic acid (for reducing the titanium); 50 mg of tartaric acid exclude the influence of 35-fold amounts of Zr^{IV} , and 50 mg of ascorbic acid in 50 ml of the solution make it possible to determine Th^{IV} in the presence of 10-fold amounts of Ti^{IV} . When large amounts of Ce^{IV} are contained (over 100-fold), it is reduced with ascorbic acid.

Equipment and Reagents

Equipment and Utensils. A Pulfrich photometer. Measuring flasks for 25 ml (6). A burette for 25 ml.

Radioactive Substances. A solution of $\text{Th}(\text{NO}_3)_4$ containing 10 $\mu\text{g/ml}$ of Th.

Reagents. Solutions: 0.05% arsenazo I; 1% ascorbic acid; 5% tartaric acid; 0.1 N HNO_3 .

Performance of Work

Introduce 10, 20, 30, 40 and 60 μg of Th in the form of a solution of $\text{Th}(\text{NO}_3)_4$ into five of the 25-ml measuring flasks. Next add to each flask 2 ml of 1% ascorbic acid, 1 ml of 5% tartaric acid, and 3 ml of a 0.05% solution of arsenazo I. Dilute the mixtures with 0.1 *N* nitric acid, bringing the volume of the solution up to the mark.

In a similar way, prepare a solution with an unknown content of Th.

Use a universal photometer to measure the optical density of the solutions with a known concentration relative to water and relative to the reagent solution. Plot light absorption curves of the optical density D versus the wavelength λ . Plot a curve of the light absorption of the reagent solution relative to water on the same graph. Measure the optical density of all the solutions at the maximum light absorption, and plot a calibration curve. Use the latter to find the amount of Th^{IV} in the control sample.

F. PHOTOMETRIC DETERMINATION OF THORIUM IN MONAZITES WITH ARSENAZO II [7]

Arsenazo II forms a blue-violet compound with the ion Th^{IV} in an acidic solution. At a molar ratio of 1 : 1, the maximum light absorption of its solutions is at 560 nm. The colour appears virtually immediately after the solutions are poured together and is stable for a prolonged period. The light absorption of the complex within the acidity limits of 0.01-0.6 *N* (with respect to HCl) varies insignificantly. The Bouguer-Lambert-Beer law is observed at a concentration not over 0.4 $\mu\text{g}/\text{ml}$.

Sulphate ions (1-5 mg/ml) partly mask Th^{IV} (by 5-7%) at an acidity of 0.2 *N* (with respect to HCl) and a reagent concentration of 10^{-4} *M*. But by introducing a definite amount of SO_4^{2-} ions into all the solutions, the error of determination can be virtually excluded. Phosphate ions have the least influence on the determination of Th^{IV} in a hydrochloric acid medium (0.1-0.4 *N*). Fluoride ions, which mask thorium, are removed sufficiently completely when monazite is decomposed by fusing with pyrosulphate. The determination is hindered by Zr^{IV} and Ti^{IV} , but their content in monazites does not exceed 0.02%, and the inter-

ference they cause may be disregarded. The determination is not hindered by cations hydrolyzing at $\text{pH} \gg 2$ (alkali and alkaline-earth metals, rare-earth elements, Al, Cu, Fe^{II} , etc., even in a 1000-fold amount).

The method makes it possible to determine 0.5-7% of Th^{IV} in monazite sands with an error of 3-5%; when the content is smaller, the Th^{IV} is separated from other elements by twofold fluoride or fluoride-oxalate precipitation.

Equipment and Reagents

Equipment and Utensils. A Pulfrich photometer or a photocolorimeter. A brazing burner. Measuring flasks for 25 and 100 ml. A pipette for 2.5 ml. A quartz test tube.

Radioactive Substances. Monazite sand. A solution of $\text{Th}(\text{NO}_3)_4$ containing 20 $\mu\text{g}/\text{ml}$ of Th.

Reagents. Ascorbic acid. Solutions: 2% $\text{K}_2\text{S}_2\text{O}_7$ in HCl (1:5), 0.1% arsenazo II; 0.5% $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$.

Performance of Work

Fuse a weighed sample of monazite sand (10-200 mg) containing over 0.5% of Th with 2 g of potassium pyrosulphate in the quartz test tube or in a porcelain crucible during several minutes, first with slight heating in the flame of the brazing burner, and then at the temperature of dark red glow. Dissolve the melt in 40 ml of dilute (1 : 1) hydrochloric acid (the prepared solution must be almost transparent and contain no heavy particles indicating the incomplete decomposition of the monazite). Transfer the solution into a 100-ml measuring flask, dilute it with water, bring the volume up to the mark, and filter part of the solution into a dry flask.

Take an aliquot part (2.5 ml) containing Th^{IV} within the limits from 25 to 100 μg with the pipette, transfer it into a 25-ml measuring flask, introduce 10-20 ml of ascorbic acid (when the monazite contains iron), 2.0 ml of a 0.5% solution of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, 5.0 ml of a 0.1% solution of arsenazo II, dilute with water (up to the mark), stir, and in five minutes measure the optical density. The reference solution must contain 5.0 ml of a 0.1% solution of arsenazo II and 2.5 ml of a 2% solution of $\text{K}_2\text{S}_2\text{O}_7$ in dilute (1 : 5) hydrochloric acid; the total volume of the solution must be 25 ml.

To plot a calibration curve, perform a series of measurements with standard solutions. For this purpose, introduce such an amount of a standard solution of $\text{Th}(\text{NO}_3)_4$ into five 25-ml measuring flasks that they will contain 20, 40, 60, 80, and 100 μg of Th^{IV} (respectively), and add to each flask 2.5 ml of a solution of $\text{K}_2\text{S}_2\text{O}_7$ in dilute (1:5) hydrochloric acid, 2.0 ml of a solution of NaH_2PO_4 , and 2 ml of a solution of arsenazo II. Dilute the solutions (up to the mark) with water, stir, after five minutes measure the optical density, and plot a calibration curve that is used to find the amount of Th^{IV} in the control solution*.

G. PHOTOMETRIC DETERMINATION OF THORIUM WITH ARSENAZO III

Arsenazo III forms an intracomplex compound with Th^{IV} ions that in its stability is superior to the compound with arsenazo I and arsenazo II. This makes it possible to determine thorium in strongly acidic solutions without the

Table 12.1. Selected Properties of Compounds of Th^{IV} with Arsenazo III

Molar ratio, Th: arsenazo III	Wavelength, maximum light absorp- tion, nm	Molar absorption coefficients	Wavelength, maximum light absorp- tion, nm	Molar absorp- tion coefficients
	At pH=3.0-1.5		At acidity of 3.5 M with respect to HCl or HNO_3	
1 : 1	620	32 300	612	41 500
	670	24 500	665	65 300
1 : 2	565	47 000	Not determined	
	675	40 000	615	94 000
1 : 3	No complex detected		665	127 000
1 : 4	No complex detected		570	64 000

preliminary separation of SO_4^{2-} , PO_4^{3-} , F^- , $\text{Cr}_2\text{O}_7^{2-}$, and other ions. The determination is also not hindered by Zr^{IV} and Nb^{V} .

* When the thorium content in the monazite sand exceeds 10-15%, the aliquot part of the solution and the amount of the 2% solution of $\text{K}_2\text{S}_2\text{O}_7$ in the dilute (1:5) hydrochloric acid are diminished accordingly.

The reagent is very sensitive. The absorption of light by the solutions greatly depends on the nature of the acid. Selected characteristics of compounds of Th^{IV} with arsenazo III are given in Table 12.1.

The following conditions are optimal for determining thorium: a concentration of HNO_3 (or HCl) of 3.5 *M*, a molar ratio of arsenazo III to thorium of 7.5. When determining thorium in nitric acid solutions, 1 g of urea should be introduced for each mole of HNO_3 to prevent oxidation of the reagent. In these conditions, a complex is formed with a molar ratio of arsenazo III to thorium of 3 and with the maximum light absorption at 665 nm (the molar absorption coefficient is 127 000).

Equipment and Reagents

Equipment and Utensils. A photocolorimeter or a Pulfrich photometer. Measuring flasks for 25 ml (6). A burette for 25 ml. A graduated cylinder for 10 ml.

Radioactive Substances. A solution of $\text{Th}(\text{NO}_3)_4$ containing 5 $\mu\text{g/ml}$ of Th^{IV} .

Reagents. Solutions: 0.05% arsenazo III; HCl (density 1.18 g/cm^3); 0.5% oxalic acid.

Performance of Work

Introduce 1, 2, 3, 4, and 5 ml (respectively) of a standard solution of $\text{Th}(\text{NO}_3)_4$ into five 25-ml measuring flasks. Add to each of the flasks 1 ml of a 0.05% aqueous solution of arsenazo III and 8 ml of concentrated hydrochloric acid (density 1.18 g/cm^3). Dilute the solutions (up to the mark) with water, stir them well, and measure their optical density in the photoelectrocolorimeter or the universal photometer. To prepare a reference solution, take the same solutions, but do not introduce any thorium compound. If Ti^{IV} (not over 10 μg) or Zr^{IV} (not over 1 mg) is present, introduce 1 ml of 0.5% oxalic acid into each of the solutions prior to their dilution.

H. PHOTOMETRIC DETERMINATION OF MICROGRAM AMOUNTS OF THORIUM WITH ARSENAZO III [11]

To determine very small amounts of thorium, a coloured compound of thorium with arsenazo III is extracted with isoamyl alcohol in the presence of diphenylguanidinium

chloride and monochloroacetic acid. The method combines the determination of thorium with its extraction concentration and makes it possible to determine it at a dilution of $1:5 \times 10^8$ (0.002 $\mu\text{g/ml}$).

Equipment and Reagents

Equipment and Utensils. An electrophotocolorimeter. Separatory funnels for 25 ml (6). A burette for 25 ml. A measuring cylinder for 10 ml.

Radioactive Substances. A solution of $\text{Th}(\text{NO}_3)_4$ containing 1 $\mu\text{g/ml}$ of Th.

Reagents. Monochloroacetic acid. Isoamyl alcohol. Solutions: 0.025% arsenazo III; 20% diphenylguanidinium chloride; 0.1 *N* HNO_3 .

Performance of Work

Introduce 1, 2, 3, 4, and 5 ml (respectively) of a standard solution of $\text{Th}(\text{NO}_3)_4$ into five 25-ml separatory funnels. Add to each of them 1 ml of a 0.025% solution of arsenazo III, then add 4, 3, 2, 1, and 0 ml (respectively) of 0.1 *N* nitric acid. Introduce into each funnel 1 g of monochloroacetic acid, 10 ml of a 20% solution of diphenylguanidinium chloride and 10.0 ml of isoamyl alcohol. Shake the mixture for 2 min, allow the phases to separate, filter off the organic layer through a paper filter into a dry planchet, and measure the optical density relative to a solution obtained in a similar way, but containing no Th^{IV} .

Process the solution with an unknown content of thorium in exactly the same way; find the amount of Th^{IV} in it according to a calibration graph.

I. PHOTOMETRIC DETERMINATION OF THORIUM WITH 1-(PYRIDYL-2'-AZO)-RESORCINOL [12]

Ions of Th^{IV} in a weakly acidic or neutral medium form with 1-(pyridyl-2'-azo)-resorcinol a compound in the molar ratio of 1:4 that is soluble in water and has an orange-red colour with the maximum absorption of light at 500 nm. The reagent itself is coloured yellow at this value of the pH and has a maximum absorption of light at 415 nm. The coloured compound forms at a pH of 3-9; the optimal conditions are created at a pH of 6.4-6.7. The molar absorption coefficient of the compound is 38 900; the equilibrium con-

stant of the reaction (at $\text{pH} = 6.4-6.7$) is 10^{-8} . The solutions obey the Bouguer-Lambert-Beer law at a content of 10-200 μg of Th^{IV} in 25 ml of the solution.

The compound of thorium with 1-(pyridyl-2'-azo)-resorcinol is more stable than thorium complexonate; conversely, the complexonates are the more stable compounds for rare-earth elements. Consequently, thorium can be determined in the presence of rare-earth elements by first adding 1-(pyridyl-2'-azo)-resorcinol (to form coloured compounds of the reagent with the ions of thorium and rare-earth elements), and then complexon III (for decomposing the complex of the reagent with the ions of rare-earth elements and forming colourless complexonates of the rare-earth elements).

The method is suitable for determining thorium in monazites and other minerals after separating the thorium in the form of the oxalate.

Equipment and Reagents

Equipment and Utensils. A photocolorimeter. Measuring flasks for 50 ml (6). A burette for 25 ml. A measuring cylinder for 25 ml.

Radioactive Substances. A solution of $\text{Th}(\text{NO}_3)_4$ containing 20 $\mu\text{g}/\text{ml}$ of Th.

Reagents. Solutions of 0.5% 1-(pyridyl-2'-azo)-resorcinol; 20% $\text{NH}_4\text{CH}_3\text{COO}$; 0.01 *M* Na-EDTA.

Performance of Work

Introduce 2 ml of a 0.05% solution of 1-(pyridyl-2'-azo)-resorcinol into each of five 50-ml measuring flasks, dilute with water to 10 ml, add 20, 40, 60, 80, and 100 μg of Th^{IV} (respectively) in the form of a standard solution of $\text{Th}(\text{NO}_3)_4$, stir, and introduce 15 ml of a 20% solution of $\text{NH}_4\text{CH}_3\text{COO}$ into each flask. Dilute the solutions (up to the mark) with water, stir them well, and measure their optical density relative to a solution of the reagent prepared in similar conditions*.

Proceed in the same way with the solution being analysed, and find the amount of Th^{IV} in it according to the calibration graph.

* When plotting the calibration curve, Na-EDTA does not have to be added to solutions containing Th and not containing rare-earth elements.

To determine thorium in monazites containing rare-earth elements, to an aliquot part of the solution containing 30-70 μg of Th^{IV} and 50-100-fold (in comparison with the thorium) amounts of rare-earth elements, add 2 ml of a 0.05% solution of 1-(pyridyl-2'-azo)-resorcinol, gradually introduce 15 ml of a 20% solution of $\text{NH}_4\text{CH}_3\text{COO}$, let the mixture stand for 10 min, stirring it from time to time, and then add dropwise, constantly stirring, 5 ml of a 0.01 M solution of Na-EDTA*.

Dilute the solution (up to the mark) with water, and after stirring measure its optical density in the conditions described for the plotting of the calibration curve.

Experiment 12.4. PREPARATION OF THORIUM BY REDUCING ThO_2 WITH CALCIUM [3, 13]

Thorium in the free state is most frequently prepared by the calcium thermal method or by the electrolysis of melts. The metal is purified using what is called a transportation reaction with transfer of the thorium in the form of the readily volatile ThI_4 .

Since thorium has a high melting point (1700°C), while its reduction occurs at a lower temperature, the thorium is produced in the form of a powder. It is then fused into a compact metal in special furnaces, or methods of powder metallurgy are used. A freshly cut cross section of pure compact thorium is a silvery white metal. Below 1400°C , thorium exists in the α -modification (a face-centered cubic lattice, $a = 0.5086\text{ nm}$). Above 1400°C , it exists in the form of the β -modification (a space-centered lattice, $a = 0.411\text{ nm}$). The density of thorium is $11.5\text{--}11.7\text{ g/cm}^3$.

Equipment and Reagents

Equipment and Utensils. A crucible or muffle furnace. A thermocouple with a pyrometer. A mechanical stirrer. A water-jet pump. A chamotte crucible. An iron crucible with a cover or a thick-walled

* 5 ml of a 0.01 M solution of Na-EDTA are sufficient for the complete fixing of 5 mg of ions of rare-earth elements reduced to the metal. If the content of the rare-earth elements in the aliquot part of the solution is known to be less than 5 mg, the amount of the added Na-EDTA solution is decreased accordingly.

iron vessel with a screwed-on lid. Chemical beakers for 1 litre (2). A Wurtz flask. A Büchner filter.

Radioactive Substances. ThO₂.

Reagents. Anhydrous CaCl₂. Metallic calcium. Ethanol. Diethyl ether. A concentrated solution of HNO₃. Charcoal.

Performance of Work

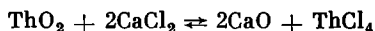
Put 20 g of ThO₂, 14 g of metallic calcium (in the form of shavings or a powder) and 20 g of anhydrous CaCl₂* into a dry vessel that can be closed. Shake the substances to obtain good mixing of the components. Place the mixture into a thick-walled iron vessel. It may be replaced with a crucible having a cover. Since the crucible cover does not close tightly, put the iron crucible into the chamotte crucible having a larger diameter and cover it with a thick layer of pulverized charcoal to prevent atmospheric oxygen from getting into the reaction mixture.

Put the thick-walled iron vessel or the chamotte crucible containing the iron one into the electric crucible or muffle furnace and hold it at 950-1000 °C for one hour. Control the temperature according to the pyrometer with the thermocouple.

Extract the cooled reaction mixture from the crucible, triturate it in a mortar, and gradually (with vigorous stirring) pour it into a beaker containing about one litre of water. After all the calcium that has failed to react with the ThO₂ reacts with the water, stop stirring, decant the liquid, and wash the solid residue 4-5 times with water (one litre portions), stirring the contents of the beaker each time for 5-10 min. In addition to Ca, the washing removes Ca(OH)₂ and CaCl₂, and also a dark powder of finely ground thorium.

Pour 100 ml of water onto the washed solid residue and

* It is presumed that the CaCl₂, which melts at the temperature of the experiment, dissolves the calcium oxide forming as a byproduct:



The CaO must be removed because it prevents the merging of the separate drops of the molten Th, which is therefore obtained in the form of a very fine powder that is lost during the following processing. On the other hand, it has been shown that the ThCl₄ formed in this reaction catalyzes the reduction process. If no CaCl₂ is introduced, a 100% surplus of metallic calcium must be added to the system.

treat it with 15 ml of concentrated nitric acid under a hood with stirring to remove the impurities fused into the reguli of metallic thorium.

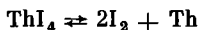
In 10 min after introducing the HNO_3 , dilute the solution with water about 10 times, and decant the liquid. Repeat the nitric acid treatment with the following dilution with water and decantation of the solution two more times. Next wash the solid residue twice with one-litre portions of water, and decant the washing water. Filter off the metallic thorium in the Büchner filter, wash it in the filter with 50 ml of ethanol, then (for complete drying) with 50 ml of diethyl ether, and, finally, heat the preparation to 300°C in a Wurtz test tube while sucking off the air with a water-jet pump.

The thorium has the form of a coarse-grained dark gray powder. The yield is about 30% of theory.

To identify the preparation obtained, register a Debye powder diagram and compare it visually with the diagrams for the standard preparation of thorium and the initial ThO_2 . Usually the thorium prepared by the calcium-thermal method contains an appreciable admixture of ThO_2 and is later refined by accretion techniques.

Experiment 12.5. REFINING OF THORIUM BY THE IODIDE METHOD [2, 13]*

Small amounts of thorium prepared, for example, by the calcium-thermal method can be purified by iodide refining. The iodine introduced into the reaction space reacts with the metallic thorium to be purified with the formation of thorium tetraiodide ThI_4 that is volatile at an elevated temperature. The tetraiodide dissociates according to the reaction



on a red-hot filament having an optimal temperature. The iodine thus transfers the thorium onto the metallic filament. Iodide refining leads to the removal of all the non-volatile impurities from the thorium and makes it possible to produce the thorium with a high purity*.

* The refining procedure described below is suitable for purifying many metals. Particularly, titanium can be refined when using this procedure (in considerably milder conditions than thorium).

Equipment and Reagents

Equipment. A heat-resistant glass vessel with tungsten incandescent filaments (Fig. 12.1). An electric furnace. An optical pyrometer. An ammeter. A voltmeter. A brazing burner.

Radioactive Substances. Metallic thorium prepared by the calcium-thermal method.

Reagents. Very pure crystalline iodine.

Performance of Work

Place 1 g of powdery metallic thorium prepared by the calcium-thermal method (Experiment 12.4) into the heat-resistant glass (Pyrex) vessel (Fig. 12.1). Connect the vessel to a vacuum installation and at a rarefaction of 0.13 Pa begin to degas the vessel. For this purpose, heat the entire arrangement except for ampoule 7 with iodine with the flame of a gas burner and then hold it for two more hours at a temperature of 500-550 °C. After degassing the vessel, raise the temperature of tungsten filaments 9 and 10 fastened in tungsten holders 3, 4, and 5 up to 1700 °C. Measure the temperature by means of the optical pyrometer. Record the values of the current and voltage at which this temperature was reached.

After cooling to 200 °C, seal off the vessel from the vacuum system at point 1. Break ampoule 7 containing 1 g of iodine with metal ball 8 that is brought into motion by the action of a magnet. After the iodine evaporates into the evacuated vessel, seal off ampoule 7 from the vessel at point 6.

Next place the vessel into the furnace, heat it to 550 °C, and heat the tungsten filaments at the same voltage and current that ensured their heating to 1700 °C in the preliminary experiment. Now the optical pyrometer will show a lower temperature because the vessel is filled with coloured iodine vapour. Maintain this temperature during the entire experiment, gradually (as the layer of metal on the filament grows) increasing the current.

When the vessel is heated to 550 °C, the iodine vapour reacts with the thorium. The volatile ThI_4 formed decomposes on the red-hot filament with the liberation of pure thorium. Hence, the iodine "conveys" the thorium onto the red-hot filament.

After growth of the thorium layer on the filament, the external heating furnace may be switched off because the heated filament will ensure the required temperature.

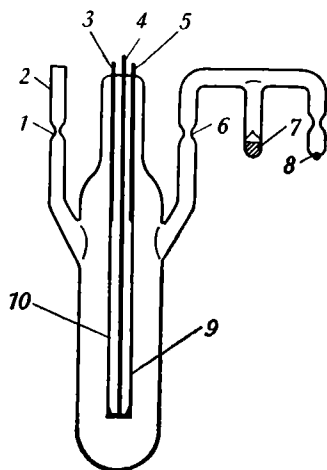


Fig. 12.1. Vessel for iodide refining of thorium:

1—place of sealing off from vacuum system; 2—place of charging thorium and connecting to vacuum installation; 3, 4, 5—tungsten conductors and holders; 6—place of sealing off ampoule; 7—ampoule with iodine; 8—metal ball (striker); 9, 10—tungsten filaments

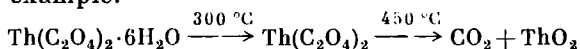
During the experiment, keep the current and voltage at values such that the product $\sqrt{IE}$ (where I is the current, A, and E is the voltage, V) characterizing the power radiated from the surface of the filaments will be 0.4-0.6. At a lower value of this product, the output of the process is low, while at a higher value the filament may burn out. At the end of the process, the current may reach 100-200 A.

Check the purity of the thorium prepared by the method of iodide refining described here (also known as the van Arquel de-Bour accretion method) by comparing the Debye powder diagrams of the initial and purified thorium with the diagrams of a standard specimen of thorium and thorium oxide. The thorium obtained, as a rule, is very pure and produces a powder diagram containing no other lines except for those of the α -modification of metallic Th.

Experiment 12.6. PREPARATION OF ThO_2 [1, 13]

Thorium dioxide, which is the starting substance for synthesizing many thorium compounds, is prepared in several ways. Most often, the reactions of decomposition of the

hydroxide, nitrate, or oxalate of thorium are used for this purpose, for example:



Thorium dioxide is a white finely crystalline powder with a density of 9.87 g/cm³ melting at 3050 °C and boiling at 4700 °C. Its crystal lattice is of the fluorite type. Greatly roasted ThO₂ is insoluble in acids. Reactive ThO₂ is prepared by decomposing thorium chloride, nitrate, or sulphate at 800 °C in a stream of superheated steam.

Equipment and Reagents

Equipment and Utensils. A muffle furnace. A sand bath. An analytical balance. A platinum crucible. A porcelain bowl.

Radioactive Substances. Crystalline Th(NO₃)₄ · nH₂O.

Performance of Work

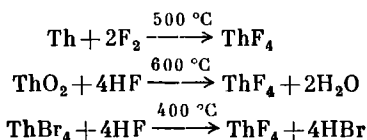
Carefully heat crystalline thorium nitrate in a porcelain bowl on the sand bath. Strong swelling of the reaction mass occurs at 300-400 °C owing to the violent evolution of nitrogen oxides and water. After the swelling stops and the danger of splashing of the material is eliminated, transfer the mass into the platinum crucible and roast it in the muffle furnace at 800-850 °C up to complete elimination of the nitrogen oxides and water. Roasting in the porcelain bowl at this temperature could lead to contamination of the ThO₂ with silicon dioxide.

Determine the yield of the ThO₂ by weighing the initial and the obtained preparations.

Experiment 12.7. PREPARATION OF THORIUM TETRAHALIDES [1, 13]

A. THORIUM TETRAFLUORIDE

Thorium tetrafluoride, used in the electrolytic production of metallic thorium, can be prepared in several ways, for example:



Only thorium tetrafluoride hydrates $\text{ThF}_4 \cdot (2.5-3.0)\text{H}_2\text{O}$ separate from aqueous solutions. Dehydration, especially detachment of the last portions of water, proceeds with difficulty and is attended by the hydrolysis of the ThF_4 . This is why methods of synthesis are preferred that allow anhydrous ThF_4 to be prepared directly.

A way of preparing anhydrous ThF_4 from ThO_2 by the action of an active fluorinating agent—Freon-12 (difluorodichloromethane) is described below.

Thorium tetrafluoride is a colourless substance melting at 1110°C and having a low volatility. It is hygroscopic, dissolves very poorly in water, hydrolyzes under its action, and transforms into the oxyfluoride ThOF_2 .

Equipment and Reagents

Equipment and Utensils. A tubular electric furnace. A pyrometer with a thermocouple. An analytical balance. A quartz tube 80 cm long and 2-3 cm in diameter. A dry chamber. A porcelain boat. U-shaped tubes.

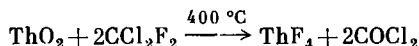
Radioactive Substances. ThO_2 .

Reagents: Freon-12; P_2O_5 .

Performance of Work

Put 3 g of ThO_2 between two glass wool wads inside the quartz tube or into the porcelain boat in the tube. Place the tube with the boat in the tubular furnace and heat the region of the quartz tube containing the boat with the ThO_2 up to 400°C . Monitor the temperature with the aid of the thermocouple connected to the pyrometer.

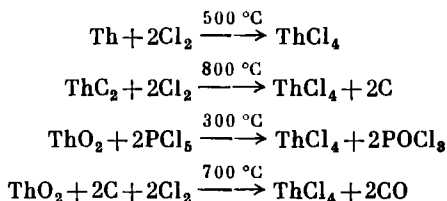
Pass a stream of Freon-12 through the tube with the ThO_2 after letting it flow through two U-shaped tubes filled with a mixture of P_2O_5 and glass wool to free it of moisture. The following reaction proceeds at 400°C :



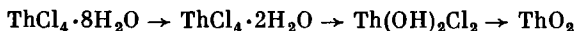
Perform fluorination during three hours under a hood. Cool the arrangement in a stream of Freon. Unload the specimen of ThF_4 from the arrangement in the dry chamber. If the ThF_4 preparation is to be stored, seal it in an ampoule.

B. ANHYDROUS THORIUM TETRACHLORIDE

Anhydrous ThCl_4 can be prepared by acting with various chlorinating agents on metallic thorium, and also on thorium dioxide, hydride, sulphide, carbide, etc. For example:



It is quite difficult to prepare the anhydrous tetrachloride from the hydrate of thorium tetrachloride ($\text{ThCl}_4 \cdot 9\text{H}_2\text{O}$ or $\text{ThCl}_4 \cdot 8\text{H}_2\text{O}$) because its heating is attended by detachment of HCl and formation of the basic salt, and then of thorium dioxide:



Thorium tetrachloride forms colourless, very hygroscopic crystals with a density of 4.59 g/cm^3 melting at 770°C and boiling at 921°C .

ThCl_4 dissociates to a considerable extent at a temperature above $1000\text{--}1100^\circ\text{C}$. It dissolves well in water, poorly in diethyl ether, and does not dissolve at all in benzene, toluene, and chloroform. The basic organic substances (alcohols, aldehydes, etc.) form numerous addition products with ThCl_4 .

Equipment and Reagents

Equipment and Utensils. A tubular electric furnace for $800\text{--}900^\circ\text{C}$. A pyrometer and a thermocouple. A quartz tube (about 1 m long, 3 cm in diameter) and a quartz air cooler and condenser secured inside it on a ground-glass joint. A pH meter with a glass electrode. Chromatographic columns of the burette type (2). A magnetic stirrer. An analytical balance. A dry chamber. A jar with a ground glass stopper for 100 ml. A chemical beaker for 100 ml. Chemical beakers for 200 ml (5). A measuring flask for 50 ml. A pipette for 5 ml. A measuring cylinder for 10 ml. Burettes for 25 ml (2).

Radioactive Substances. ThO_2 .

Reagents. Rod sulphur. Dry gaseous chlorine. Dry CO_2 , 20 g of the cation exchanger KU-2 in the Na^+ form. Solutions: 10% ammonium acetate; 1% K_2CrO_4 ; 0.1 M AgNO_3 ; 0.1 M NaCl .

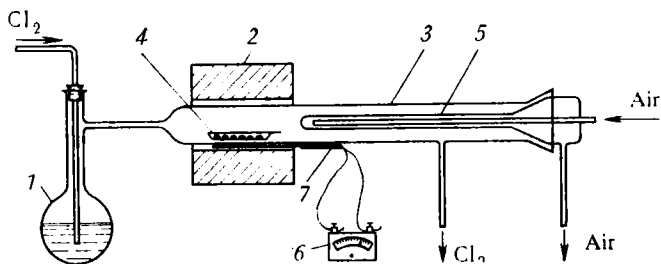


Fig. 12.2. Arrangement for preparing anhydrous ThCl_4 :
 1—Wurtz flask; 2—tubular electric furnace; 3—reaction tube; 4—porcelain boat with ThO_2 ; 5—quartz air cooler; 6—pyrometer; 7—thermocouple

Performance of Work

Assemble the arrangement shown schematically in Fig. 12.2. Put a weighed portion of thorium dioxide (20 g) in porcelain boat 4 into quartz tube 3 inserted into tubular electric furnace 2. Connect Wurtz flask 1 to tube 3. Put pieces of rod sulphur into flask 1 and connect it to a source of dry chlorine.

Pass a stream of chlorine through the reaction tube and simultaneously heat the sulphur in the Wurtz tube. A vapour of an active chlorinating agent—sulphur chloride S_2Cl_2 —enters the reaction tube. Chlorinate the ThO_2 for two hours, maintaining a temperature of 700–800 °C in the reaction space. The anhydrous ThCl_4 sublimes and settles on quartz air cooler 5 inserted into the reaction tube on a ground-glass joint. The surplus of Cl_2 , and also the S_2Cl_2 and SO_2 are discharged under a hood or are absorbed by a solution of alkali.

Upon the completion of chlorination, cool the arrangement in a stream of chlorine. Next put cooler 5 together with the reaction tube into the dry chamber, clean off the sublimate into a weighing bottle with a clean glass rod, close the bottle with a ground-glass stopper, and then coat it with paraffin.

Analyse the product obtained for its content of thorium and chlorine. For this purpose, dissolve an accurately weighed* portion of the preparation (2 g) in water

* Transfer the amount of the preparation needed for analysis into a preliminarily weighed separate weighing bottle in the dry chamber and weigh it together with the bottle on the analytical balance.

transfer the solution into the 50-ml measuring flask and add water, bringing the volume of the solution up to the mark. Thoroughly stir the solution and take two samples with the pipette for determining thorium and two samples for determining chlorine. Determine the thorium in accordance with Experiment 12.3. To determine the chlorine, proceed as follows.

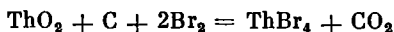
First separate the thorium ions from the chloride ones so that the former will not hinder the argentometric determination of the chlorine. For this purpose, fill the two small glass columns of the burette type with 10 g of the cation exchanger KU-2 in the Na^+ form. Introduce 5 ml of the ThCl_4 solution into each column and wash with 100 ml of distilled water. The filtrate contains chloride ions and sodium ions. The thorium ions hindering the determination are sorbed by the cation exchanger. Before repeated use, the resin in a column must be washed with a 1% Na-EDTA solution to remove the thorium, transformed into the sodium form (by passing a solution of NaCl through it), and thoroughly washed with distilled water to remove the unabsorbed salts.

Determine the chlorine in both filters by using, for example, Mohr's method. It is based on the fact that the indicator K_2CrO_4 forms a red precipitate with the added silver ions only after all the chloride ions are precipitated in the form of AgCl .

Into each of the 200-ml beakers containing the samples being analysed (with an approximate volume of 100 ml), introduce 5 ml of a 10% solution of ammonium acetate (buffer), next about 1 ml of a 1% solution of K_2CrO_4 (chemically pure)—an indicator, and slowly, while stirring well, add a titrated 0.1 *M* solution of AgNO_3 . Add the last drops of the AgNO_3 very slowly until an unvanishing red colour appears. Next add an accurate 0.1 *M* solution of NaCl until the colour vanishes. Subtract the volume of the NaCl used from that of the AgNO_3 (the molarity of these solutions must be the same). Obtain the chlorine content in the sample by multiplying the difference obtained by the molarity of the solution. To determine the content of chlorine in the initial sample, multiple this number by 10. Compare the found chlorine content in the ThCl_4 with that calculated according to the formula.

C. ANHYDROUS THORIUM TETRABROMIDE

Anhydrous thorium tetrabromide ThBr_4 can be prepared by acting with phosphorus tribromide vapour on thorium hydride, sulphide, or carbide, or by the reaction



Anhydrous thorium tetrabromide cannot be prepared by the dehydration of thorium tetrabromide hydrate $\text{ThBr}_4 \times 12\text{H}_2\text{O}$ because already at 50°C it transforms into $\text{Th}(\text{OH})\text{Br}_3 \cdot \text{H}_2\text{O}$, and at 105°C , into ThOBr_2 .

Thorium tetrabromide is a colourless, hygroscopic crystalline substance with a density of 5.6 g/cm^3 melting at 679°C and boiling at 857°C . It dissolves well in water and ethanol.

Equipment and Reagents

Equipment and Utensils. A tubular furnace. A thermocouple with a pyrometer. An arrangement for bromination (see Fig. 11.3, p. 62). A dry chamber. A jar for 10 ml with a ground-glass stopper.

Radioactive Substances. ThO_2 .

Reagents. Dry bromine. Dry nitrogen. Powdered charcoal.

Performance of Work

Perform bromination in a quartz arrangement (see Fig. 11.3, p. 62). Thoroughly mix a weighed portion of ThO_2 (10 g) preliminarily roasted during one hour at 800°C in a mortar with 20 g of powdered charcoal. Pour the mixture in a uniform layer into the heated part of reaction quartz tube 4 so that the layer of the substance occupies about three-fourths of the tube section, while one-fourth of the reaction space remains free.

Displace the air from reaction tube 4 with dry nitrogen, heat furnace 3 to $800\text{--}900^\circ\text{C}$, and roast the reaction mixture in a stream of N_2 until the vapour of the adsorbed water stops evolving. Carefully remove the water condensed on the unheated parts of the tube by heating the tube with the flame of a gas burner. After this, insert quartz air cooler 6 into tube 4 and attach absorber 5 (freeze out the surplus of the bromine or absorb it with a solution of an alkali).

Close cock 2 and open cock 7, thus passing a stream of N_2 through flask 1 with dry Br_2 that is first dried over P_2O_5 . Place a two-fold surplus of bromine in comparison with

the stoichiometric amount into flask 1. Slowly pass the nitrogen through the bromine (one bubble an hour), the latter being carried by the nitrogen into the reaction space.

Perform bromination during four hours at 900 °C. Cool the arrangement in a stream of bromine to prevent dissociation of the ThBr_4 at the elevated temperature. Next displace the bromine with nitrogen (open cock 2 and close cock 7).

Introduce cooler 6 on which crystals of ThBr_4 condensed after sublimation together with the reaction tube into the dry chamber. Clean off the ThBr_4 crystals from the cooler with a dry glass rod into the jar and close the latter with its ground-glass stopper. Determine the yield of the ThBr_4 .

D. ANHYDROUS THORIUM TETRAIODIDE

Thorium tetraiodide ThI_4 is one of the most volatile compounds of thorium. It is used in the refining of metallic thorium.

Equipment and Reagents

Equipment and Utensils. A heat-resistant glass tube with constrictions (Fig. 12.3). A fore pump. A brazing burner. Gas burners. A thermocouple with a pyrometer. A chemical beaker for 100 ml.

Radioactive Substances. Metallic powdery thorium.

Reagents. Crystalline iodine. A solution of HNO_3 (1:1). Absolute ethyl ether.

Performance of Work

Perform the synthesis in a heat-resistant glass (Pyrex) tube with constrictions (Fig. 12.3). Treat the metallic powdery thorium in the 100-ml beaker with dilute HNO_3 (1:1) to remove the oxide film, then wash it with water and dry with absolute ether. Introduce a weighed portion of thorium (2 g) treated in this way into middle part 6 of the glass tube (through 3). Seal the extension of the tube through which the thorium was introduced.

Close the inlet to tube 2 with a rubber stopper. Connect the end of the tube to the fore pump, evacuate the air from the arrangement, and perform degassing by heating the glass of the tube with the flame of a gas burner. Next disconnect the vacuum, open the stopper, and introduce 10 g of pure iodine into the arrangement. After this, seal the arrangement at point 2. Cool part 1 of the tube with dry ice,

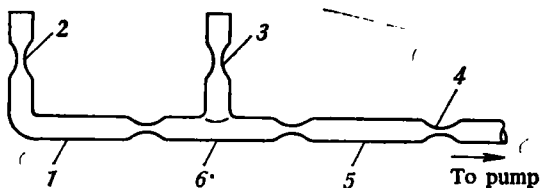


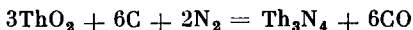
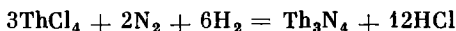
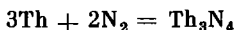
Fig. 12.3 Arrangement for preparing anhydrous ThI_4

evacuate the arrangement, and at a pressure of 0.13 Pa seal it at point 4. Next heat the middle 6 of the tube with the flame of a burner to 525°C , monitoring the temperature by means of the thermocouple with the pyrometer.

Alternately heat parts 1 and 5 of the tube with the flame of a gas burner and cool them with air without stopping to heat part 6. As a result, the iodine and the ThI_4 are made to travel from one end of the tube to the other and pass several times over the heated thorium. Perform the reaction up to the complete conversion of the thorium to ThI_4 , make the latter pass into part 5 of the tube, and seal the tube.

Experiment 12.8. SYNTHESIS OF Th_3N_4 [13]

Thorium nitride Th_3N_4 can be prepared in several ways, for example



Thorium nitride is a black-brown powder stable in dry air and readily soluble in acids.

Equipment and Reagents

Equipment and Utensils. A tubular electric furnace. A thermocouple with a pyrometer. A quartz tube. A porcelain boat. A jar for 100 ml with a ground-glass stopper.

Radioactive Substances. Metallic thorium (fine shavings or a powder).

Reagents. Dry nitrogen.

Performance of Work

Put a weighed sample (1 g) of the metallic thorium into the boat and the latter into the quartz (or porcelain) tube heated by the tubular electric furnace. Displace the air from the tube with dry nitrogen, bring the temperature in the reaction space up to 800 °C, and, monitoring the temperature by means of the thermocouple with the pyrometer, pass the nitrogen through during three hours. Cool the preparation in a stream of dry nitrogen. Determine the yield of the Th_3N_4 .

Store the Th_3N_4 in the 100-ml. jar with the ground-glass stopper or in a sealed ampoule.

Experiment 12.9. PREPARATION OF SOLUBLE THORIUM SALTS AND DETERMINATION OF THEIR COMPOSITION [1, 2, 13]

The nitrate, sulphate, and chloride are typical thorium salts soluble in water. They are widely used in technological and analytical practice.

A. HYDRATES OF $\text{Th}(\text{NO}_3)_4$

Thorium nitrate forms a large number of hydrates of various composition: $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$, $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$, and $\text{Th}(\text{NO}_3)_4 \cdot 12\text{H}_2\text{O}$. The solubility of thorium nitrate in water at 25 °C is 65.6% (by mass) when calculated for the anhydrous salt. The anhydrous nitrate also dissolves in ethers, alcohols, and ketones. An aqueous solution of $\text{Th}(\text{NO}_3)_4$ has an acidic reaction because of hydrolysis. Thorium nitrate hydrates detach water at a temperature below 100 °C. Above 150 °C, the $\text{Th}(\text{NO}_3)_4$ decomposes with the evolution of nitrogen oxides. At 500 °C, the thorium nitrate transforms into ThO_2 .

Equipment and Reagents

Equipment and Utensils. A continuous balance. A Büchner filter. A water bath. Chemical beakers for 500 ml (3). Porcelain bowls (2).

Radioactive Substances. A 2% solution of $\text{Th}(\text{SO}_4)_2$ or any other soluble salt of thorium.

Reagents. Solutions: 25% NH_4OH ; HNO_3 (1:1).

Performance of Work

Treat a definite volume (200 ml) of a 2% solution of $\text{Th}(\text{SO}_4)_2$ with a surplus of 25% NH_4OH . Wash the precipitate of the hydroxide $\text{Th}(\text{OH})_4$ in the Büchner filter until the SO_4^{2-} ions disappear in the washing water.

Dissolve the freshly precipitated $\text{Th}(\text{OH})_4$ with heating in the minimum amount of HNO_3 (1 : 1). Divide the solution of $\text{Th}(\text{NO}_3)_4$ into two approximately identical parts. Evaporate one part on the water bath up to the beginning of crystallization. Let the second half of the solution evaporate in a porcelain bowl at room temperature.

Filter off the crystals separated in both vessels and dry them in the air. Determine the hydrate composition of each of the hydrates by dehydration on the continuous balance. In dehydration, heat at a rate of 3 K/min from room temperature to about 600 °C. Determine the substance obtained as a result of such heat treatment, the formation of what compounds the separate steps on the curve of the mass of the substance against the temperature correspond to, and the composition of the thorium nitrate hydrates separated from the aqueous solution.

B. CRYSTAL HYDRATE OF $\text{Th}(\text{SO}_4)_2$

Equipment and Reagents

Equipment and Utensils. A continuous balance. A Kurnakov pyrometer. A Büchner filter. A sand bath. A porcelain bowl or crucible. A porcelain mortar. Chemical beakers for 250 ml (3).

Radioactive Substances. ThO_2 .

Reagents. A concentrated solution of H_2SO_4 .

Performance of Work

Treat a weighed portion (5 g) of ThO_2 in the porcelain bowl or crucible with concentrated sulphuric acid while heating on the sand bath. Remove the surplus H_2SO_4 by evaporating the solution until dry, but not permitting roasting of the dry residue, which would lead to decomposition of the thorium sulphate. Repeat the treatment with sulphuric acid and the removal of its surplus twice. Triturate the solid anhydrous $\text{Th}(\text{SO}_4)_2$ containing no admixture of acid salts (because evaporation is performed up to the disappear-

ance of the H_2SO_4 vapour) into a powder and slowly introduce the latter with stirring into 50 ml of icy water. Treat the undissolved residue after drying once more with H_2SO_4 , as described above, and then again with icy water.

Heat the thorium sulphate solution to 30-35 °C. The precipitate formed will be the almost pure octahydrate containing only an insignificant admixture of $\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$. If the solution is evaporated at 30-35 °C, virtually the entire thorium sulphate crystallizes in the form of the octahydrate. Suck out the crystals of $\text{Th}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ in the Büchner filter, wash them with ethanol, and dry them in the air at room temperature.

Determine the hydrate composition of the crystals. For this purpose, use the continuous balance to plot a curve of the loss of mass of the preparation with elevation of the temperature. Use a heating rate of 2-4 K/min. Determine the temperature at which water is detached and the temperature of dissociation of the thorium sulphate into ThO_2 and SO_3 (acquaint yourself with the published data). Compare the thermogravigram obtained on the continuous balance with the thermogram plotted by means of the Kurnakov pyrometer at the same heating rate and for the same temperature interval.

C. OCTAHYDRATE OF ThCl_4

Crystal hydrates of thorium tetrachloride are known with 8, 7, 4, and 2 water molecules. The octahydrate, the procedure for whose preparation is described below, is a colourless crystalline substance diffusing in the air and well soluble in water and ethanol.

Equipment and Reagents

Equipment and Utensils. A continuous balance. A Kurnakov pyrometer. A Büchner filter. An arrangement for preparing gaseous HCl . A water bath or an infrared lamp for evaporating solutions. Chemical beakers for 250 ml (3). Chemical beakers for 500 ml (2). A jar for 100 ml with a ground-glass stopper.

Radioactive Substances. $\text{Th}(\text{NO}_3)_4 \cdot n\text{H}_2\text{O}$.

Reagents. Diethyl ether. Solutions: 25% NH_4OH ; concentrated HCl ; 6 *M* HCl .

Performance of Work

Treat thorium hydroxide prepared from a solution of $\text{Th}(\text{NO}_3)_4$ or $\text{Th}(\text{SO}_4)_2$ by the action of NH_4OH and completely washed with water (in the Büchner filter) to remove admixtures of anions of the initial salt with a surplus of concentrated HCl . Evaporate the solution of ThCl_4 under the infrared lamp (or on the water bath) to the consistency of a syrup and cool to room temperature. Filter off the precipitated crystals in the Büchner filter and then dissolve them in a minimum amount of 6 *M* hydrochloric acid. Cool the solution to 0 °C and saturate it with gaseous HCl . Next add an approximately equal volume of diethyl ether to this solution and continue to pass a stream of HCl through the mixture until the water and ether layers stop separating. Filter off the precipitated colourless crystals and wash them with ether in the Büchner filter. Store them in the 100-ml jar with the ground-glass stopper.

Establish the content of water in the prepared hydrate according to the thermogravimetric curve plotted with the aid of the continuous balance. Use a 0.5-g sample for dehydration and heat it at a rate of 2-4 K/min. Compare the thermogravigram with the thermogram obtained when heating a sample in the Kurnakov pyrometer. Determine the temperature at which hydrolysis of the hydrated thorium chloride begins.

Experiment 12.10. PRECIPITATION OF THORIUM IN THE FORM OF SPARINGLY SOLUBLE SALTS [1, 2, 13]

The following sparingly soluble compounds are used to separate thorium from impurities, and also for its quantitative separation from solutions: hydroxides, the peroxide, oxalates, iodate, phosphates, fluoride, molybdate, and also certain derivatives of organic compounds such as cupferonate, hydroxyquinolate, and phenyl arsenate.

A. THORIUM PHOSPHATES

Thorium orthophosphate is soluble in acids, therefore thorium is most often determined and separated by precipitating its pyrophosphates and hypophosphates that do not dissolve even in strong acids. Preference is given to the

precipitation of the pyrophosphate $\text{ThP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ because, unlike the hypophosphate $\text{ThP}_2\text{O}_6 \cdot 11\text{H}_2\text{O}$, it forms large crystals and its precipitate is well filtered off.

Thorium pyrophosphate dissolves in solutions of ammonium oxalate and carbonate. Boiling of a solution of ThP_2O_7 with a solution of NaOH leads to the formation of $\text{Th}(\text{OH})_4$.

Equipment and Reagents

Equipment and Utensils. A continuous balance. A Büchner filter. A chemical beaker for one litre.

Radioactive Substances. A solution of a thorium salt (0.3 g of thorium in 100 ml of the solution).

Reagents. Solutions: saturated aqueous of SO_2 or 10% $\text{Na}_2\text{S}_2\text{O}_3$; $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ (10 g in one litre of water).

Performance of Work

Place a definite volume (100 ml) of a solution containing 0.3 g of thorium in the form of any soluble salt in the one-litre beaker and add water up to 800 ml (the solution must be 0.3 *M* relative to the mineral acid).

Heat the solution up to boiling with stirring and add 5 ml of a saturated aqueous solution of SO_2 or several drops of a 10% solution of $\text{Na}_2\text{S}_2\text{O}_3$ to reduce the usual impurities ($\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$, $\text{F}^{3+} \rightarrow \text{Fe}^{2+}$). Next add 30 ml of a solution of $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ (10 g in one litre of H_2O) to the solution. Boil it with stirring for 5 min, immediately filter off the precipitate, wash it with a small amount of water, and dry in the air.

Determine the content of water in the air-dry substance by dehydrating 0.2 g of the preparation on the continuous balance. Note the temperature of complete dehydration. Determine the thorium content in the anhydrous residue (its composition?). For this purpose, dissolve the substance with boiling in an ammonium oxalate solution and determine the thorium in it complexonometrically (see Experiment 12.3B and C).

Compare the calculated and experimentally found content of Th and H_2O .

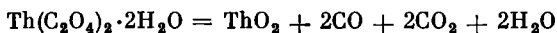
B. THORIUM OXALATES

Depending on the reaction conditions—the ratio of the amounts of reactants, the concentration, temperature, and pH of the solution, thorium and oxalate ions can form com-

pounds differing in their composition and solubility in water. Particularly, jelly-like poorly filtering precipitates and large crystal ones with excellent filtration may be obtained.

Thorium oxalates must be precipitated for analytical and technological purposes from solutions of mineral acids, because in weakly acidic, neutral, and alkaline solutions the solubility of thorium oxalate increases owing to the formation of complex compounds of the type $[\text{Th}(\text{C}_2\text{O}_4)_{2+n}]\text{Me}_{2n}^{\text{I}}$ having a high solubility. When precipitating thorium from solutions containing a large surplus of a mineral acid, the possibility of the formation of compounds with a mixed anion must be taken into account. For example, the oxalatochloride $\text{ThCl}_2(\text{C}_2\text{O}_4) \cdot n\text{H}_2\text{O}$ precipitates from hot strong solutions of hydrochloric acid. To obtain the normal thorium oxalate in such conditions, a fivefold surplus of oxalic acid must be taken for precipitation.

Normal thorium oxalate has the composition $\text{Th}(\text{C}_2\text{O}_4)_2 \times \times 6\text{H}_2\text{O}$. Four water molecules can be removed by heating the preparation to 120°C or by drying it in a desiccator over H_2SO_4 . Roasting of the dihydrate at $600\text{--}650^\circ\text{C}$ leads to formation of the dioxide:



Further dehydration of the dihydrate $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ proceeds with difficulty. For example, upon heating to 160°C , complete dehydration of the $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 0.75\text{H}_2\text{O}$ still does not occur. Solid thorium oxalate is assumed to have a dimer structure $[\text{Th}(\text{C}_2\text{O}_4)_2]_2$ and its low solubility is associated with this circumstance.

The solubility of thorium oxalate hexahydrate in water at 25°C is (when calculated for ThO_2) 0.07 mg/litre . The solubility of thorium oxalate is somewhat higher in mineral acids than in water, but is still comparatively low. For example, in 1 N nitric (or hydrochloric) acid, its solubility (when calculated for ThO_2) is $20\text{--}30\text{ mg/litre}$, and in 1 N sulphuric acid at 25°C it is 120 mg/litre .

Equipment and Reagents

Equipment and Utensils. A continuous balance. An analytical balance. A desiccator with concentrated H_2SO_4 . A Büchner filter. A chemical beaker for 500 ml . A porcelain bowl.

Radioactive Substances. $\text{Th}(\text{NO}_3)_4 \cdot n\text{H}_2\text{O}$.

Reagents. A saturated solution of oxalic acid.

Performance of Work

To a hot solution of 20 g of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ in 80 ml of water acidified with HNO_3 to $\text{pH} = 1$, add with stirring a surplus of oxalic acid in the form of a saturated solution (8 g of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in 80 ml of water). After cooling the mixture to room temperature, better after letting it stand overnight, filter off the precipitate, wash it with water, and dry it in the air.

The yield of $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ is 16 g. Transfer part of the precipitate into the porcelain bowl and dry it to a constant mass in the desiccator over H_2SO_4 .

Dry a portion (0.5 g) of thorium oxalate (hexahydrate, and then partly dehydrated in the desiccator), weighed on the analytical balance, on the continuous balance. Determine whether the molecules of the crystallization water have the same bond strength in the thorium oxalate hydrates, whether the nature of the dehydration curve depends on the rate of heating of the preparation, and at what temperature the thorium oxalate decomposes.

Compare the mass of the ThO_2 obtained upon roasting the thorium oxalate with the mass of the initial preparation. Use the curve of continuous weighing to determine the hydrate composition of the thorium oxalate.

Experiment 12.11. SEPARATION OF UX_1 (^{234}Th) FROM URANIUM SALTS [14]

The natural isotope ^{232}Th is inconvenient for performing many radiochemical and analytical experiments owing to its low specific activity and the complications involved in the quantitative registration of α -radiation. The use of another natural isotope of this element— β -radioactive ^{234}Th (UX_1) appearing upon the decay of ^{238}U makes it possible to circumvent these difficulties. Although the energy of the β -particles of ^{234}Th is low (the values of E_{max} equal 0.103 and 0.193 MeV), the activity of ^{234}Th preparations is measured quite simply according to the considerably harder β -radiation of its daughter isotope UX_2 (^{234}Pa). The half-life of UX_2 is 1.175 min, and radioactive equilibrium between the UX_1 and UX_2 sets in in 12-15 min.

The extraction of ^{234}Th from uranium salts stored for at

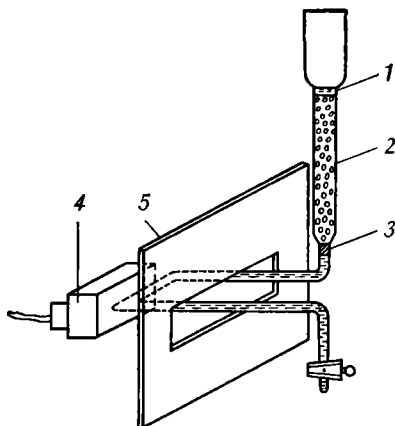


Fig. 12.4 Column for ion-exchange separation of UX_1 :
1—solution; 2—resin; 3—glass wool wad; 4—counters; 5—lead screen

least half a year can be performed in various ways. The method described below has a good reproducibility and ensures a high extraction of ^{234}Th .

Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window counter. A chromatographic column combined with a radiometric instrument (Fig. 12.4); the working part of the column has an internal diameter of 15 mm and a length of 20 cm. Separatory funnels for 50 and 500 ml. Measuring cylinders for 10, 50, and 500 ml. Porcelain bowls for 50 (3) and 500 ml (3). A vacuum desiccator. A water bath. A lamp for evaporation. Glass beakers for 1 litre (2) and 100 ml (3). A glass rod. A funnel. A bowl for measuring activity.

Radioactive Substances. $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ stored for at least half a year.

Reagents. Cation-exchange resin KU-2 with a grain size of 50-100 mesh. Diethyl ether. Solutions: HNO_3 (1:1), 2 M; 8 M and 10 M HCl ; 0.5 M $\text{H}_2\text{C}_2\text{O}_4$; 30% H_2O_2 ; 0.1 M NaSCN .

Performance of Work

Preliminarily prepare the resin for introduction into the column by repeatedly treating it with 100-ml portions of 8 M hydrochloric acid for removing the Fe^{3+} and other impu-

rities. Continue the treatment up to a negative reaction of the washing solution with the 0.1 *M* solution of NaSCN. Carefully transfer the washed resin in the form of a suspension in a hydrochloric acid solution of the same concentration into the column until the height of the cation exchanger in it reaches 16-18 cm. Remember that bubbles of air in the cation exchanger must not be tolerated. In the course of separation, there should always be a layer of liquid over the resin.

Dissolve a portion of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in dilute (1:1) nitric acid. If the object of the experiment is the separation and identification of UX_1 , use 0.25 g of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 5 ml of HNO_3 for the experiment. When it is desired to separate UZ from the obtained UX_1 , dissolve 10-12 g of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 50 ml of HNO_3 . Transfer this solution into a separatory funnel and add diethyl ether to it. The volume of the funnel and that of the added ether are, respectively, 50 and 30 ml, 500 and 400 ml. (*When working with diethyl ether, extinguish all the gas burners in the laboratory!*) Thoroughly stir the mixture in the funnel by repeated shaking. Fasten the funnel in a stand, and after separation of the liquid remove the aqueous (lower) phase into a glass beaker, and drain off the ether solution into a special vessel. Repeat the extraction process. Collect all the ether extracts containing uranyl nitrate for regeneration of the uranium (losses are impermissible). Put the ether extracts in the vacuum desiccator and evacuate the latter up to complete evaporation of the ether (to accelerate the evaporation of the ether, place the lower part of the desiccator in a pan with water heated to 35 °C).

Pour off the pale yellow aqueous phase into a porcelain bowl and carefully evaporate it on the water bath for removal of the ether. Add concentrated (10 *M*) hydrochloric acid to the solution until the HCl concentration in it is 8 *M*, after which pass it through the chromatographic column at a rate of 0.5-1.0 ml/min. The thorium is sorbed by the resin, while the uranium passes into the filtrate in the form of a chloride complex. After this, wash the column five times with 2 *M* hydrochloric acid (the volume of each portion is not to be less than the free volume of the column) for complete removal of the uranium. Gather all the filtrates containing uranium, evaporate them, and hand in the separated salt to the laboratory assistant.

Wash out the UX_1 from the column with a 0.5 *M* solution of oxalic acid at a washing rate of 0.5 ml/min. Control the completeness of separation with the aid of the radiometric instrument.

Evaporate the eluate to a volume of 10-15 ml, after which add to it 10 ml of nitric acid and 10 ml of hydrogen peroxide needed to decompose the oxalic acid. Evaporate the solution till dry, next add 10 ml each of the nitric acid and the hydrogen peroxide to the residue, and repeat evaporation of the solution.

To identify the isotope, dissolve the residue in the bowl after evaporation in 2-5 ml of 2 *M* hydrochloric acid and transfer the solution into the bowl for measuring the activity. Evaporate the solution under the lamp until dry and determine the activity of the preparation. Measure the counting rate during a month, controlling the stability of operation of the counter installation with the aid of a uranium preparation. Determine the half-life of the separated isotope and compare the found value with tabulated data.

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Chapter 13 The Chemistry and Analysis of Radioactive Isotopes—Decay Products of Uranium and Thorium

Polonium [1, 2]

All work with polonium is performed in a sealed glove box for work with α -active preparations. The equipment and utensils needed for performing the given investigation must be introduced into the chamber through the transfer lock and remain there up to termination of the work. For greater safety, surgeon's gloves should be worn in addition to the gloves of the box. During work, the doors of the transfer lock must be closed. After work, all the polonium preparations must be handed in and the box cleaned of possible contaminants.

Experiment 13.1. SEPARATION OF Po FROM EQUILIBRIUM MIXTURE RaD-RaE-RaF [1]

Polonium is usually obtained in microamounts from old ampoules containing radon in which after the virtually complete decay of the radon a radioactive precipitate remains that consists of RaD, RaE, and RaF. Polonium can be separated from a mixture of these isotopes by coprecipitation with tellurium compounds after reduction with SnCl_2 . Upon reduction with SO_2 , the polonium is reduced only to the divalent state and does not coprecipitate with tellurium compounds.

Equipment and Reagents

Equipment and Utensils. A counter with a scintillation detector of α -radiation. A counter for measuring β -radiation. A sealed glove box for working with α -radioactive substances. A centrifuge. A jasper mortar. A water bath. A balance. A lamp for evaporation. Pipettes for 3 ml (2). Glass rods (2). Small quartz beakers (3). A watch glass. Standard glass bowls.

Radioactive Substances. An old ampoule containing ^{222}Rn [$\sim 40 \text{ MBq}$ ($\sim 1 \text{ mCi}$) calculated for radon] or a solution of a long-lived deposit of radon.

Reagents. TeO_2 . SO_2 (in a cylinder). Solutions: 10 M and concentrated HCl ; concentrated HNO_3 ; 1.5 M SnCl_2 .

Performance of Work

Carefully crush an old ampoule containing radon in the mortar. Carefully transfer the crushed glass into a small quartz beaker, pour in 20-30 ml of aqua regia, and heat on the water bath after covering with the watch glass. Upon single-fold heating with aqua regia, 50-70% of the long-lived active deposit passes into the solution. Part of the radioactive atoms, owing to the phenomenon of recoil upon the decay of the parent radioactive nuclei, penetrate into the glass, and for their extraction threefold prolonged boiling with fresh portions of aqua regia is required.

After the treatment with aqua regia, pour over the solutions containing RaD - RaE - RaF into a small quartz beaker and slowly evaporate until dry on the water bath (*perform evaporation carefully owing to the volatility of polonium at elevated temperatures*).

Treat the residue after evaporation with 2-4 ml of 10 M HCl (3 times), rubbing the bottom of the beaker with a glass rod; transfer the solution into a centrifuge test tube and evaporate it on the water bath to a volume of 1-2 ml. Next transfer into it about 0.1 g of TeO_2 and add an equal volume of a 1.5 M solution of SnCl_2 . Centrifuge the solution with the precipitate formed in it; extract the liquid with a pipette, transfer it into a standard glass bowl and carefully evaporate it. The absence of activity when measuring with the α -scintillation counter points to the completeness of coprecipitation of the polonium with the tellurium.

Thoroughly wash the precipitate with water (3 times) to remove the bismuth and lead compounds that may have precipitated together with the tellurium, and then dissolve it in 2 ml of concentrated nitric acid.

To separate the polonium from the tellurium, carefully evaporate the solution until dry on the water bath in a small quartz beaker and dissolve the dry residue in 2-3 ml of concentrated hydrochloric acid. Transfer the solution into a centrifuge test tube, dilute it to 5 M relative to the HCl, and pass a stream of SO₂ through it during 10-15 min. The tellurium will be reduced to the elementary state and precipitate, while the polonium in the divalent state will remain in the solution. Centrifuge the precipitate. Remove the solution over the precipitate with a pipette into standard glass bowls and carefully evaporate them under a lamp at 60-70 °C. Carry the bowls out of the glove box. Check your gloves and hands in an α -dosimeter.

Measure the radioactivity of the polonium in the α -scintillation counter. Check the purity of separating the polonium from RaE according to the absence of β -radioactivity when measuring in the β -counter. Since RaD has soft β -radiation, check the absence of lead in the solution in about 5-10 days according to the radiation of the RaE that forms from the parent RaD.

Identify the polonium according to the path of its α -rays in the air or to the energy of its α -radiation.

Radium [3]

Experiment 13.2. QUANTITATIVE DETERMINATION OF ²²⁶Ra ACCORDING TO RADON [4-6]

The content of ²²⁶Ra in specimens can be determined according to the amount of ²²²Rn accumulated during a definite time. The accumulation of ²²²Rn from ²²⁶Ra corresponds to the case of the formation of a radioactive isotope whose decay constant is much larger than that of the parent substance. Owing to the comparatively low rate of decay of ²²⁶Ra, it may be considered that ²²²Rn accumulates at a constant rate.

The change in the amount of ²²²Rn in time is determined by the equation

$$\frac{dq}{dt} = m\Delta - \lambda q \quad (13.1)$$

where q is the amount of ²²²Rn contained in the vessel by the instant t , m is the mass of the ²²⁶Ra, g , Δ is the amount

of ^{222}Rn formed from 1 g of ^{226}Ra in unit time, and λ is the decay constant of ^{222}Rn .

Here the first term is the accumulation, and the second, the decay of the ^{222}Rn . Solving this equation provided that for $t = 0$ we have $q = q_0$, we obtain

$$q = q_0 e^{-\lambda t} + \frac{m\Delta}{\lambda} (1 - e^{-\lambda t}) \quad (13.2)$$

If we preliminarily remove all the ^{222}Rn from the preparation of ^{226}Ra , at the instant of termination of radon separation ($t = 0$), we have $q_0 = 0$, and Eq. (13.2) acquires a simpler form:

$$q = \frac{m\Delta}{\lambda} (1 - e^{-\lambda t}) \quad (13.3)$$

For ^{222}Rn , the term $e^{-\lambda t}$ practically vanishes when $t = 30$ days. This corresponds to the accumulation of an equilibrium amount of radon ($t = t_\infty$):

$$q_\infty = \frac{m\Delta}{\lambda} \quad (13.4)$$

Hence, the amount of ^{222}Rn accumulated by the instant t can be expressed in terms of the equilibrium amount of ^{222}Rn by the formula:

$$q = q_\infty (1 - e^{-\lambda t}) \quad (13.5)$$

If we assume, as is usually done in practice, that the activity of 3.7×10^{10} Bq (1 Ci) of ^{222}Rn corresponds to its amount in equilibrium with 1 g of $^{226}\text{Ra}^*$, then $q_\infty = m$, which allows us to write

$$m = \frac{q}{1 - e^{-\lambda t}} \quad (13.6)$$

This formula shows the relation between the mass of ^{226}Ra (in g) and the activity of ^{222}Rn expressed in Bq for any instant.

When determining the amount of ^{222}Rn according to the ionization current, it is assumed that 3.7×10^{10} Bq of emanation in equilibrium with the active deposit yields a saturation current equal to 6.21×10^6 electrostatic units.

* The error made here depends on the values of the radioactive constants of ^{226}Ra and ^{222}Rn used in calculating the equilibrium amounts of the isotopes.

Corrections have to be made to obtain the absolute amount of ^{222}Rn according to the ionization current:

(1) for the incomplete utilization of the α -rays of ^{222}Rn and the products of its decay in the ionization chamber (the Duan correction):

$$a = \frac{1}{1 - 0.572 (S_c/V_c)} \quad (13.7)$$

where S_c is the internal surface area of the chamber, and V_c is its volume;

(2) for failure to achieve the saturation current (usually about 10%):

$$b = 0.1$$

Consequently, if the saturation current corresponds to the rate of change in the potential dv/dt , while the capacity of the instrument is C , the amount of ^{222}Rn is

$$q = C \frac{dv}{dt} \frac{1}{300 \times 60} \frac{1}{1 - 0.572 (S_c/V_c)} (1 - b) \frac{10^{-6}}{6.21} \quad (13.8)$$

When measuring the activity of the ^{222}Rn (in MBq) in a pulse-ionization chamber,

$$q = \frac{I}{k_\alpha} \times 10^6 \quad (13.9)$$

where I is the registered counting rate (without the background), and k_α is the counting coefficient of the α -radiation of ^{222}Rn and the products of its decay; for a standard litre chamber, $k_\alpha = 1.2$.

The method of determining the content of ^{226}Ra by comparing with a standard is more accurate.

The effect produced by ^{222}Rn in an ionization or scintillation chamber is proportional to its amount, therefore the content of ^{226}Ra can be determined quantitatively by comparing the effects produced by the ^{222}Rn in the solution being studied and in a standard specimen with a known content of ^{226}Ra .

If measurement is performed on an electrometer (according to the speed of the filament), the standard specimen is used to find the value of an electrometer graduation in grammes of ^{226}Ra . Next the same chamber and the same electrometer are used to determine the content of ^{226}Ra in the solution being studied. When ^{222}Rn is introduced into the cham-

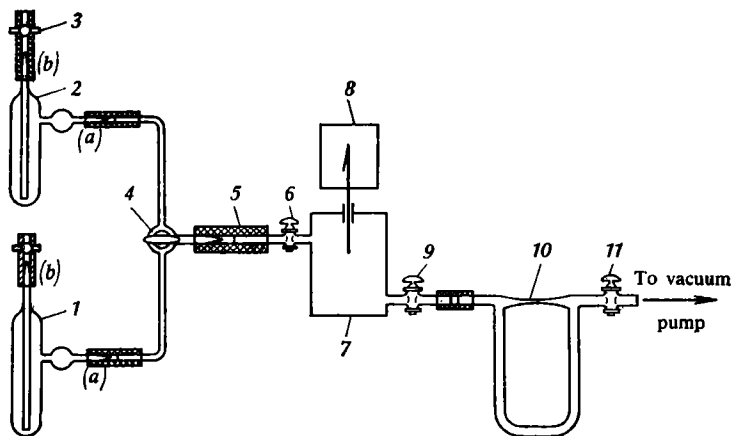


Fig. 13.1

Arrangement for determining radium, thorium, actinium, and uranium according to emanations:

1—bubbler with standard solution; 2—bubbler with solution being studied; 3—rubber tube with clamp; 4—three-way cock; 5—tube with drying agent; 6, 9, 11—two-way cocks; 7—emanation chamber; 8—electrometer or counter for registering α -activity of gases; 10—rheometer or rotameter for 0.2-2 or 1.0-5.0 litre/min

ber, the ionization current during three hours increases as a result of the formation of radioactive products of radon decay. A further change in the ionization current occurs slowly. Consequently, to obtain comparable results, it is recommended either to perform all the measurements at the same time, or reduce their results to a three-hour value.

When working with a pulse or scintillation chamber, usually only the three-hour counting rate is measured. The best results can be achieved if after admitting the ^{222}Rn into the pulse ionization chamber it is kept for three hours under a direct voltage (minus on the central electrode), and then the measurements are performed.

Equipment and Reagents

Equipment. An arrangement for determining radium according to emanations (Fig. 13.1; rheometer 10 is not needed for the given experiment). A vacuum pump.

Radioactive Substances. Hydrochloric acid solutions, standard and the one being investigated, in bubblers (10^{-7} - 10^{-9} g of ^{226}Ra in 5% hydrochloric acid).

Performance of Work

(a) Graduation of Arrangement

Check the sealing of the emanation chamber. Assemble the arrangement for determining radium according to emanation (Fig. 13.1). Measure the background of the arrangement.

After closing access to both bubblers by means of cock 4, evacuate the air from chamber 7 to a pressure of 4×10^3 Pa with cock 6 open. Close cock 9, and then for one instant by turning cock 4 connect bubbler 1 to chamber 7 to create a rarefaction in the connecting tubes. Close cocks 6 and 4, and after this open the ends of the tubes of bubbler 1 with the standard solution: first end *a* under the rubber tube fitted onto the sealed tip of the ampoule and gripped with a clamp, then *b* also under a rubber tube with a clamp. It is good practice to introduce a thin wire beforehand into the rubber tube with clamp 3 fitted onto end *b* of bubbler 1 (or in the following, of bubbler 2); this helps to monitor the rate of flow of the air passing through the bubbler. Next carefully open cock 6 and turn three-way cock 4 so that a small stream of air (about 100 bubbles a minute) passes through bubbler 1 and entrains the ^{222}Rn from the bubbler into the chamber (cock 9 remains closed). Continue the blowing 10-20 min until the pressure in the chamber becomes equal to atmospheric pressure, i.e. until bubbling of the air through the solution in the bubbler stops.

After blowing is completed, close cock 6 and disconnect the bubbler. Immediately seal the bubbler with the solution of ^{226}Ra . Record on a tag the time of completion of blowing (month, day, hour). This is needed to know the time of accumulation of ^{222}Rn when performing the following measurement.

Begin measurement of the time spent by the ^{222}Rn in the emanation chamber in 5 min after opening tube *b* and beginning to blow in air. Record the time when the measurement was begun and during three hours measure the ionization current on the electrometer (or record the rate of counting in the registering instrument). During the first half hour, perform the measurements every five minutes, and then every 20 minutes until a constant value of the ionization current (or counting rate) is achieved.

The measurements in the region of the maximum value of

the ionization current (the rate of counting) are the most accurate, therefore in practice the activity is often measured in three hours after introducing the radon into the chamber. With shorter intervals, reduce the obtained values to a three-hour current according to the relevant curve or table.

Upon the completion of the measurements (but not later than in five hours after introducing the ^{222}Rn), remove the ^{222}Rn from the chamber by evacuating the air with a pump during 10-15 min (using a good draught!). The chamber, as a rule, is not used immediately after its evacuation because the background in it remains increased for a certain time owing to the presence of an active deposit of ^{222}Rn . Since the active deposit mainly forms on the central electrode, the metal case on it can be changed only after air has been blown through it. Seal the bubbler, write on its tag the time of termination of air blowing, and hand it in for storage.

Use the measurement results to calculate the value of an electrometer graduation or the number of grammes of ^{226}Ra per count by means of the formula

$$a = \frac{m_{\text{st}} (1 - e^{-\lambda t})}{\bar{I}_{\text{st}}} \quad (13.10)$$

where m_{st} is the radium content in the standard specimen, g, and $\bar{I}_{\text{st}}$ is the mean value of the three-hour current.

Enter the results of the measurements and calculations for the standard solution and the one being investigated in the form of a table as shown below:

Standard specimen No.	
Contains	g of ^{226}Ra
Sealed (date and time)	
^{222}Rn introduced into chamber (date and time)	
Duration of accumulation	
Natural scattering (background):	
before experiment	
after experiment	
average	

Entry No.	Time of introducing radon into chamber, min	Ionization current (activity) without background, grad/min (cpm)	
		measured	reduced to three-hour value, I_1
		Mean value $\bar{I}$	

The accuracy of radon measurement by the registering instrument is appraised according to the deviation of the values of I_1 reduced to a three-hour value from $\bar{I}$.

*(b) Determination of ^{226}Ra Content
in a Solution Being Studied*

To determine the radium content in a solution being studied, transfer it into bubbler 2 (the volume of the solution and its acidity must be the same as for the standard solutions) and pass air through it for 20-30 min to remove the ^{222}Rn . Pull back the ends of the bubbler tubes and seal them. Write the time of completion of blowing on the tag. Let the solution stand for the accumulation of ^{222}Rn for several days. Further proceed as in graduation of the arrangement. Since the ionization effect of the standard solution and the specimen being studied is determined in absolutely identical conditions, all the corrections associated with the influence of the shape and dimensions of the chamber are eliminated.

Evaluate the content of ^{226}Ra in the solution m_x (in g) by the formula:

$$m_x = \frac{a\bar{I}}{1 - e^{-\lambda t}} \quad (13.11)$$

where a is the value of a scale graduation or of one registered count in grammes of ^{226}Ra , $\bar{I}$ is the ionization current reduced to the three-hour value, or the three-hour rate of counting (without the background), t is the duration of radon accumulation in the solution being studied, days, and λ is the decay constant of radon, day^{-1} .

Calculate the relative value of the ionization current for each measurement time, taking its maximum value (the value of the three-hour current) as unity.

Using the mean values of the three-hour current in the electrometer and the corresponding corrections [see formula (13.7)], calculate the absolute amount of radon in the solution being studied, and then the equilibrium content of radium. When determining the amount of radon, use formula (13.8), and calculate the equilibrium mass of the radium.

After completing work, pour the solutions of ^{226}Ra into a special jar under a hood. Thoroughly wash the bubbler with a 10% solution of Na-EDTA in a 10% solution of

Na_2CO_3 , next with hydrochloric acid with the carrier BaCl_2 , and with water, after which hand it in to the laboratory assistant. Scavenge the chamber well for the complete removal of the ^{222}Rn .

Experiment 13.3. QUANTITATIVE DETERMINATION OF ^{235}U AND ^{232}Th ACCORDING TO ACTINON AND THORON [4]

The emanation method for the quantitative determination of the content of natural radioactive radium isotopes is the most accurate one even when small amounts of ^{235}U and ^{232}Th (see the radioactive series) are in equilibrium with the radium isotopes in the material being investigated. In this case, the content of the ^{235}U and ^{232}Th is determined, respectively, according to thoron (^{220}Rn) or actinon (^{219}Rn).

Owing to the short lifetime of ^{220}Rn and ^{219}Rn , they cannot be measured by introducing them into a chamber and then registering the activity, as is done for ^{222}Rn (see Experiment 13.2). The short-lived emanations must be continuously introduced into the measuring chamber with the aid of a stream of gas whose rate of flow ensures the maximum value of the activity being registered. For this purpose, for example, a continuous stream of air is blown through the preparation being studied that contains the radioactive isotopes ThX (^{224}Ra) or AcX (^{223}Ra) forming short-lived emanations. The air carries the latter into the measuring chamber.

The emanations are determined in the arrangement shown in Fig. 13.1.

The registered activity I of the emanation is expressed as follows:

$$I = I_0 \eta \left[\exp \left(-\lambda \frac{V_1}{\omega} \right) - \exp \left(-\lambda \frac{V_1 + V_2}{\omega} \right) \right] \quad (13.12)$$

where I_0 is the amount of emanation formed in the preparation per second (expressed in units of saturation current or counting rate), η is the emanation utilization factor (the fraction of the emanation entrained by the air stream), λ is the decay constant of the emanation, V_1 is the volume of the system from the bubbler to the ionization chamber, V_2 is the volume of the chamber, and ω is the volume rate of flow of the air stream presumed to be laminar.

The volume rate of flow of the air stream ensuring the

maximum registered activity can be found experimentally or calculated by the formula

$$\omega_{\text{opt}} = \lambda V_2 \ln \left(\frac{V_1 + V_2}{V_1} \right) \quad (13.13)$$

The content of ^{235}U and ^{232}Th in the specimen being studied is determined by the method of comparison with a standard specimen containing a known amount of uranium or thorium, or of the relevant radium isotope (^{224}Ra , ^{223}Ra). In measurements according to thoron, the standard is a solution containing a known amount (1-10 mg) of ^{232}Th in equilibrium with the decomposition products, for example a solution of a primary mineral containing thorium. In measurements according to actinon, the standard is a solution of a uranium mineral in which the mean ratio $^{235}\text{U} : ^{238}\text{U} = 0.007$ is not violated. The solution should contain about 10 mg of uranium.

Equipment and Reagents

Equipment. An arrangement for measuring emanations (see Fig. 13.1). A vacuum pump. A bubbler with 5% HCl.

Radioactive Substances. Preparations containing ^{235}U , ^{232}Th , ^{227}Ac , or ^{228}Th , to be studied and standard [~ 370 -3.7 Bq (10^{-8} - 10^{-10} Ci)].

Performance of Work

(a) Determining Optimal Rate of Flow of Air Stream

Using formula (13.13), appraise the optimal rate of flow of the air stream, having calculated the values of the chamber volumes V_2 and the sum of the air volumes in the bubbler, drier, and connecting tubes V_1 . Determine the optimal rate of flow of the air stream experimentally. For this purpose, measure the ionization current (rate of counting) produced by the radiation of the emanation entrained by the air from the bubbler at various rates of flow of the air stream.

First measure the background of the arrangement (see Fig. 13.1) at the appraised rate of flow of the air. For this purpose, instead of bubbler 1 with the standard solution, connect a bubbler with an inactive solution, switch over cock 4 to this bubbler, and with cocks 6, 9, and 11 closed,

connect the arrangement to the vacuum pump. Next open cocks 6 and 11, and then, carefully, cock 9 to prevent throwing out of the liquid from rheometer 10, set the calculated rate of flow of the air ω_{opt} , and measure the background. After this, to measure the activity of the solution, without touching cock 9, close cock 11 and switch over cock 4 to bubbler 2 containing a solution of thorium or uranium.

Open cock 11, if necessary again regulate the rate of flow of the air with cock 9, and in 3-5 min begin a measurement. Measure the activity at least three times.

Before passing over to measurement at a different rate of flow of the air, scavenge the chamber with air because a certain amount of the emanation remained in it. To do this, close cock 11, switch over cock 4 to the bubbler with the inactive solution, and again open cock 11. Practically, it is sufficient to scavenge the chamber for five minutes to restore the initial value of the background.

Next set a different rate of flow of the air stream, connect the bubbler with the active solution, and measure the ionization current (the counting rate) corresponding to the set rate of flow of the air. In measurements with thoron, vary the rate of flow of the air from 0.1 to 1.0 litre/min, and with actinon, from 0.5 to 2 litre/min.

Enter the measurement results in a table of the following form:

Rate of flow of air through solution being studied ω , litre/min	Ionization current (counting rate) I , cpm	Mean value of ionization current (counting rate) $\bar{I}$, cpm

Next plot the ionization current (counting rate) $\bar{I}$ versus the rate of blowing through air. Choose the optimal rate of flow of the air stream at which the further measurements are to be performed.

(b) Determining the Content of ^{235}U or ^{232}Th in a Solution

A solution with a known content of uranium or thorium is used to standardize the arrangement. Connect the bubbler with the standard solution (see Fig. 13.1) to the arrangement.

Measure the ionization current (counting rate) $\bar{I}_{st}$ at least three times at the rate of flow of the air stream corresponding to the maximum ionization current (counting rate).

Next instead of the bubbler with the standard solution, connect the one with the solution being studied, determine the ionization current (counting rate) $\bar{I}_x$ at the same rate of flow of the air.

Evaluate the content of thoron and actinon in the measured preparations by the formula

$$m_x = m_{st} \frac{\bar{I}_x}{\bar{I}_{st}} \quad (13.14)$$

When analyzing natural specimens, the solution being studied may simultaneously contain three radium isotopes: ^{226}Ra , ^{224}Ra (ThX), and ^{223}Ra (AcX). When measuring the activity transferred into the chamber by the air stream, the effect produced by the radium emanation (^{222}Rn) is negligibly small, while the contribution of the activities of the thoron and actinon depends on the rate of flow of the air stream. To determine each of the activities, measurements are needed at two rates of flow of the air, and then the corresponding system of two equations must be solved, namely:

$$\left. \begin{aligned} I_1 &= (K_{Th})_1 m_{Th} + (K_{Ac})_1 m_{Ac} \\ I_2 &= (K_{Th})_2 m_{Th} + (K_{Ac})_2 m_{Ac} \end{aligned} \right\} \quad (13.15)$$

where I_1 and I_2 are the ionization current (counting rate) at two rates of flow of the air stream, and K_{11} and K_{12} are the thoron and actinon utilization factors at the corresponding rates of flow of the air.

The coefficients K_{ij} are found by preliminarily measuring the standard solutions in the corresponding conditions. When choosing these conditions, one must take into account that in one minute thoron decays by about one-half, and actinon completely.

Experiment 13.4. SEPARATION OF RADIUM ISOTOPES FROM NATURAL OBJECTS [5]

Radioactive ores or salts containing uranium and thorium are sources of radium isotopes. The present experiment describes the procedures for separating and measuring the radium isotopes ^{226}Ra , ^{228}Ra (MsTh₁), ^{224}Ra (ThX), and ^{223}Ra (AcX).

A. SEPARATION OF ^{226}Ra

Radium-226 ($T_{1/2} = 1590$ years) is separated from uranium ores after their decomposition by coprecipitation with barium salts. The quantitative determination is performed according to the emanation ^{222}Rn (see Experiment 13.2).

Equipment and Reagents

Equipment and Utensils. An electrometer or an arrangement for the quantitative determination of emanations according to their α -radiation (see Fig. 13.1). A crucible furnace for 800°C . Iron crucibles with a capacity of 20 and 100 ml (2 each). Ashless filters (large-size and small-size pore paper). A porcelain beaker for 1 litre. Heat-resistant beakers for 100, 300, and 500 ml. A measuring flask for 100 ml. Bubbler (2). A small funnel for a bubbler. A conical funnel.

Radioactive Substances. A standard preparation in a bubbler containing 10^{-9} g of ^{226}Ra . Uranium ore containing about 1-10% of uranium.

Reagents. Melted KOH. Anhydrous Na_2CO_3 . Solutions: 2.5% Na_2CO_3 ; 5% BaCl_2 ; 5 and 10% HCl containing no SO_4^{2-} ions; 5% H_2SO_4 ; a 10% solution of Na-EDTA in a 10% solution of soda.

Performance of Work

Prepare the utensils for work. For this purpose, wash the internal surface of the iron crucibles used for melting the ore several times with hot 5% hydrochloric acid. If the utensils were previously used for work with radium, preliminarily wash them thoroughly with hot 5% hydrochloric acid. Thoroughly prepare the bubblers for work. Fill them with hot 5% hydrochloric acid with an addition of BaCl_2 and boil them on a water bath. After removal of the washing solution, connect the bubblers to a water main faucet and pass a strong stream of water through them for a prolonged period.

No special chemical purity of the reagents is needed, but give attention to their radiochemical purity, and check the reagents used, especially the hydrochloric acid, for the presence of sulphate ion. Commercial fluxes (alkali, soda) may be used. Preliminarily melt the alkali to get rid of moisture that causes swelling and sputtering of the flux.

When determining small amounts of radium, check its content in the reagents, for which purpose perform what is called a "cold test" (all operations without the radioactive substance).

Calculate the amount of BaCl_2 to be used as the carrier on the basis of the following considerations. If BaSO_4 is precipitated from a solution with a volume of 200 ml, in this volume of water after precipitation there remains dissolved 4×10^{-4} g of BaSO_4 , therefore the amount of BaCl_2 must be 0.05-0.10 g.

Place a weighed sample of uranium ore (0.5-3 g) into an iron crucible and add 0.05-0.1 g of BaCl_2 , 25 g of melted KOH, and 5 g of Na_2CO_3 . Put the crucible with the mixture in the slightly heated crucible furnace, and then gradually raise its temperature to 600-700 °C. Melt the mixture during one or two hours, seeing that no melt is thrown out of the crucible. After this, extract the crucible with tongs from the furnace (*carefully!*) and cool it in air.

Cover the cooled crucible with a lid, knock at its walls with a hammer to break up the melt into pieces and transfer them into a heat-resistant beaker (with a capacity of 500-1000 ml). Carefully add hot water to the beaker (300 ml), in which all the soluble part of the melt (the remaining alkali, soda, soluble silicates, etc.) dissolves. After this add another 200 ml of boiling water and boil the mixture with good heating during 10-15 min. During the boiling, a well coagulated precipitate of carbonates will form. Stir the solution to prevent its splashing out during the boiling. To prevent the precipitation of silicic acid, when cooling the solution filter it almost boiling through a coarse filter.

Gradually wash the precipitate of carbonates on the filter with small portions of a 2.5% hot soda solution with a total volume of 0.8-1 litre. The precipitate can also be washed by decanting. In this case, decant the solution from the precipitate through a filter, then add small portions of a boiling 2.5% soda solution to the beaker and decant again. Repeat this operation many times (see that the washing solution remains hot all the time). Next transfer the precipitate onto a filter (do not transfer the scale at the bottom of the beaker onto the filter, but treat it with 5-10 ml of concentrated hydrochloric acid and later add this solution to the basic hydrochloric acid one).

Wash off the main mass of the precipitate from the filter into a beaker with a minimum amount of hot water from a wash bottle. Dissolve the precipitate remaining on the filter with hot 5% hydrochloric acid into the same beaker; bring the acidity of the solution with respect to the HCl

up to 5%. Heat the solution and precipitate BaSO_4 , adding dropwise 10 ml of 5% sulphuric acid. Boil the solution with the precipitate 10-15 min, having closed the beaker with a lid. Let the precipitate settle during one hour on a water bath and a few more hours in the cold, after which filter it off through a dense filter (small-size pore paper).

Dry the filter with the precipitate, carefully incinerate it, and roast the precipitate in an iron crucible. After cooling, melt the precipitate with a mixture of 5 g of KOH and 1 g of Na_2CO_3 until a transparent melt forms. Next extract the crucible and cool it. Transfer the melt into a beaker (200-300 ml) and add 100-150 ml of hot distilled water. Boil the precipitate 5-10 min, next filter it off, wash with a hot 2.5% soda solution until a negative reaction is obtained for SO_4^{2-} , and dissolve on the filter in a minimum amount of a hot 5% solution of HCl. Evaporate the solution to a volume of 20-30 ml and transfer it into a bubbler, in which the amount of radium is then determined by the emanation method (see Experiment 13.2).

If the obtained solution of BaCl_2 is turbid, reprecipitate the BaSO_4 with the following transfer of it into a soluble compound by melting with a mixture of Na_2CO_3 and KOH. The solution should retain its transparency during the time of measurement. Should crystals of BaCl_2 precipitate in the solution, evaporate it until dry (to remove the acid), and then dissolve the precipitate in 5% hydrochloric acid.

B. SEPARATION OF ^{228}Ra

The radium isotopes belonging to the thorium series, namely, ^{228}Ra ($T_{1/2} = 6.7$ years) and ^{224}Ra ($T_{1/2} = 3.64$ days) can be separated from thorium salts stored for a sufficiently long time. Since ^{224}Ra decays comparatively rapidly, already in a month virtually pure ^{228}Ra (MsTh_1) remains.

The quantitative determination of ^{228}Ra is performed according to the hard β -radiation of its decay product— ^{228}Ac (MsTh_2).

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. A platinum crucible. A porcelain bowl with a watch glass. A bowl for measuring activity.

Radioactive Substances. Thorium ore or a thorium compound stored for a long time.

Reagents. BaCl_2 . Hydrofluoric acid. A concentrated solution of H_2SO_4 .

Performance of Work

For ore, preliminarily assay the thorium content according to the total α -radiation. Calculate the weight of a sample containing 50-100 mg of Th.

Add 10-20 mg of BaCl_2 to the weighed sample of the ore or a thorium salt. Decompose monazite by prolonged heating with concentrated sulphuric acid (several portions) with stirring in the closed bowl. After treating the sulphates with water cooled with ice, filter off the insoluble sulphates and silicic acid. If there is a lot of silicic acid, remove it by treating the mixture with hydrofluoric acid in the platinum crucible. Filter off the barium sulphate precipitate containing ^{228}Ra through a dense filter and wash it with 200 ml of a warm solution of 5% hydrochloric acid, and then with ether or acetone. Transfer the precipitate from the filter to the preliminarily weighed bowl for measurement. After pouring in a small amount of ether, uniformly distribute the precipitate with the aid of a glass rod over the bowl.

After evaporation of the solvent, weigh the bowl and calculate the thickness of the barium sulphate layer in mg/cm^2 .

Use an end-window or cylindrical counter with a detector of β -radiation to measure the total β -activity due to the soft radiation of the ^{228}Ra and the hard β -radiation of the ^{228}Ac accumulating from it. By repeating the measurements after 24 hours, convince yourself that radioactive equilibrium has been reached between these isotopes. Using the measured value of the equilibrium activity, calculate the absolute activity of each of the isotopes by formula (0.2) in Vol. 1, taking into account the characteristics of the β -radiation, the thickness of the preparation layer, the thickness of the counter walls, and the geometric coefficient of radiation registration.

On the basis of the known thorium content in the initial preparation, calculate the degree of separation of ^{228}Ra according to the given procedure.

C. SEPARATION OF ^{224}Ra

Radium-224 is separated from radiothorium— RdTh (^{228}Th), from which ^{224}Ra is obtained as a result of α -decay. When separated with a carrier, ^{224}Ra is usually precipitated together with barium sulphate; without a carrier, ^{224}Ra can be separated from ^{228}Th by means of ion exchange or extraction. The quantitative determination of ^{224}Ra is performed according to thoron, as described in Experiment 13.3.

Equipment and Reagents

Equipment and Utensils. An arrangement for measuring the activity of thorium emanation (see Fig. 13.1)*. A counter with a detector of β -radiation. Polyethylene chromatographic columns 14 cm long and 1 cm in diameter (2). Chemical beakers for 100 ml (2). A micropipette. Centrifuge test tubes (2). A measuring cylinder for 25 ml. A conical flask for 250 ml. A funnel.

Radioactive Substances. A hydrochloric acid solution (2*N* with respect to HCl) containing ^{228}Th (RdTh) with an activity of about 37 mBq/ml ($\sim 10^{-6}$ Ci/ml). A solution containing ^{234}Th with a specific activity of 5000 and 10 000 cpm/ml.

Reagents. Solutions: 10% BaCl_2 ; 1 *N* H_2SO_4 ; 10% Na-EDTA in a 10% solution of Na_2CO_3 , 2 *N* HCl; concentrated HNO_3 ; 5% $\text{Ce}(\text{NO}_3)_3$; 10% $\text{H}_2\text{C}_2\text{O}_4$; 2% $(\text{NH}_4)_2\text{C}_2\text{O}_4$. Cation exchanger KU-2 in the H^+ form. Anion exchanger AV-17 or amberlite-410 in the $\text{C}_2\text{O}_4^{2-}$ form.

Performance of Work

(a) Precipitation with BaSO_4

Pour 0.1 ml of a solution of ^{228}Th containing an equilibrium amount of ^{224}Ra into 10 ml of 5% HCl. Next add 0.2 ml of a 10% solution of BaCl_2 . Heat the solution until it boils and precipitate sulphates by adding 5-10 ml of 1 *N* sulphuric acid.

Close the beaker with a watch glass and place it for two hours on a water bath. Next cool it for two hours with icy water, centrifuge, and wash the precipitate several times with 2 *N* hydrochloric acid. Transfer the combined filtrates by decantation into bubbler 2 (see Fig. 13.1). Dissolve the precipitate remaining in the tube in 10 ml of a 10% solution of Na-EDTA in a 10% solution of soda with heating

* Bubbler 1 with the standard solution must contain an exactly known (5-10 mg) mass of thorium-232 in equilibrium with the decay products.

and transfer the mixture into the same bubbler, adding the portions used to wash the tube. Consecutively measure the ionization current from the thorium emanation flowing from bubbler 1 with the standard solution and bubbler 2 at the same rate of flow of the air stream, monitored by rheometer 10. Repeat the measurements every 3-6 days during a month.

Plot curves of the change in the activities and calculate the equilibrium activity of the ^{224}Ra . Considering that in the initial preparation the ^{228}Ra is in equilibrium with the ^{228}Th , assay the degree of separation of the radium isotope.

(b) Chromatographic Method of Separation

Separation is based on the different sorption by the anion exchanger of the radium in the form of a cation and of the thorium bound in an oxalate complex.

Prepare the columns with the cation and anion exchangers for operation (see Experiment 3.1).

To 10 ml of 2 *N* hydrochloric acid add 0.1 ml of a solution containing $^{228}\text{ThCl}_4$ and 1 ml of a solution containing ^{234}Th as an indicator whose β -radiation is used to watch the behaviour of the ^{228}Th . Pass the solution through the column with the cation exchanger KU-2 to free it of admixtures of foreign cations, mainly Fe^{3+} .

Wash the resin with 50 ml of water and desorb the thorium with a 0.15 *M* solution of $(\text{NH}_4)_2\text{C}_2\text{O}_4$. Register the β -activity of the solution flowing out of the column as described in Chapter 3 (Vol. 1), or take samples in the test tubes for measurement using a scintillator with a well.

Pass the combined filtrates containing thorium and radium isotopes through the column with the anion exchanger AV-17 in the $\text{C}_2\text{O}_4^{2-}$ form, and collect fractions of 10 ml each for measuring ^{224}Ra according to its thoron content. Wash the column with 50 ml of water, and then desorb the thorium by passing 30 ml of 2 *N* HCl through it. Hand in the active filtrate to the laboratory assistant.

Use the data obtained in measuring the activity of the thoron to plot a curve of the activity of the filtrate fractions against the volume of the eluate. Retain half of the fraction with the maximum ^{224}Ra content to measure the half-life for identification purposes and to assay the radiochemical purity of the separated product.

Take 5 ml of the solution from each of the remaining fractions. Destroy the oxalates by boiling with 2 ml of concentrated nitric acid, add 1 ml of a 5% solution of $\text{Ce}(\text{NO}_3)_3$ to each solution, heat to boiling, and precipitate the ^{228}Th + ^{234}Th together with the cerium by adding 5 ml of 10% oxalic acid to each solution.

Measure the β -activity of the precipitates. Appraise the degree of separation of the thorium and radium isotopes.

D. SEPARATION OF ^{223}Ra

Radium-223 is separated together with barium from a solution containing ^{227}Th (radioactinium) obtained in the decomposition of uranium ores.

Equipment and Reagents

Equipment and Utensils. An installation for measuring the activity of actinium emanation (see Fig. 13.1). A heat-resistant beaker for 150 ml. A micropipette.

Radioactive Substances. A solution containing ^{227}Th with an activity of 3.7×10^3 Bq (0.1 $\mu\text{Ci/ml}$).

Reagents. Solutions: 1% $\text{Ce}(\text{NO}_3)_3$; 10% BaCl_2 ; 2 N HCl.

Performance of Work

Introduce a solution containing ^{227}Th (1 ml) into a beaker with 10 ml of 2 N hydrochloric acid, add 0.2 ml of a 10% solution of $\text{Ce}(\text{NO}_3)_3$ (an anticarrier), and 0.2 ml of a 10% solution of BaCl_2 . Precipitate the barium sulphate, with which the radium is also precipitated, and transfer the salt into a solution as described in Sec. C of the present experiment.

Determine the amount of ^{223}Ra according to the emanation of actinium (see Experiment 13.3).

Experiment 13.5. SEPARATION OF ^{223}Ra AND ^{228}Th FROM THORIUM PREPARATIONS [5]

Thorium salts, thorium dioxide, or crude sulphates obtained in the processing of thorium-containing minerals can be used as the initial preparations. If the initial substances are stored without chemical processing at least five years, decay products must accumulate in them according to the

diagram of radioactive decay of the ^{232}Th series; 1 kg of ^{232}Th (upon radioactive equilibrium with the decay products) corresponds to 3.7 MBq (0.1×10^{-3} Ci).

Equipment and Reagents

Equipment and Utensils. An installation for measuring the activity of emanation (see Fig. 13.1). Beakers for 1 litre, 0.5 litre, and 25 ml. A quartz or platinum bowl.

Radioactive Substances. A thorium preparation (thorium nitrate, thorium oxalate, or thorium dioxide) containing ~ 200 mg of Th when calculated for the metal.

Reagents. Diethyl ether or amyl acetate. Solutions: HNO_3 (1 : 1), 10% BaCl_2 ; 1 *N* H_2SO_4 ; 1.5 *N* and 3 *M* HCl ; 1% FeCl_3 , 10% NH_4Cl .

Performance of Work

Dissolve a weighed portion of the thorium preparation (~ 200 mg of the element)* with heating in dilute (1 : 1) hydrochloric acid. To the solution, diluted to an HCl content of 1.5 *N*, add 2 ml of a 10% solution of BaCl_2 . By adding 10 ml of 1 *N* sulphuric acid, precipitate radium-barium sulphates from the hot solution. In a few hours or days filter off the precipitate of sulphates and wash it with 5% hydrochloric acid. Collect the washing water; it contains about half of the adsorbed ^{228}Th , practically without a carrier.

Dry the radium-barium sulphate precipitate and place it in prolonged storage for accumulating ^{228}Th . After time has elapsed** sufficient for the accumulation of appreciable amounts of ^{228}Th , perform the operations described below.

Crude radium-barium sulphates obtained in the processing of minerals containing thorium and uranium can also be used for extracting ^{228}Th . The maximum amount of ^{228}Th accumulates from ^{226}Ra in about five years, which can readily be confirmed by calculations.

Transfer the radium-barium sulphates into a solution either by fusing with $\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$ (5 : 2), or by treating

* If thorium dioxide is used as the initial material, it must be converted into thorium sulphate, the hydroxide precipitated, and dissolved in hydrochloric acid. Process the thorium salt solution as described below.

** Since the time needed for accumulation is long, previously prepared radium-barium sulphates may be used.

the precipitate two or three times with a 10% solution of sodium-potassium carbonates by boiling during an hour.

Treat the melt with hot water, filter off the precipitate of carbonates, and dissolve it in a minimum amount of hot hydrochloric acid containing no SO_4^{2-} ions. Determine the content of ^{228}Ra in the solution according to the β -radiation (see Experiment 13.4B) and of ^{228}Th according to the thoron (see Experiment 13.3). To separate the ^{228}Th , add 200 mg of FeCl_3 to the solution and precipitate the Fe^{3+} with ammonia or pyridine. Filter off the precipitate of $\text{Fe}(\text{OH})_3$, wash it with ammonia water, and dissolve it in hydrochloric acid (1 : 1). The solution contains radiothorium together with iron. To separate the ^{228}Th without the carrier, add a tenfold surplus of NH_4CNS , and extract the thiocyanate complex of iron with diethyl ether (or amyl acetate) up to complete decolorization of the solution. Evaporate the colourless solution and roast it in a platinum or quartz crucible to remove the ammonium salts. After this treat the walls of the vessel with a small amount of hot 10% sulphuric acid. Determine the content of radiothorium (^{228}Th) in the solution.

During a month, periodically measure the activity of the thorium emanation (^{220}Rn) in samples of the solutions. Plot curves of the change in the amount of ^{224}Ra and use them to calculate the content of radium and thorium isotopes. Appraise the degree of achieving equilibrium between the isotopes ^{228}Th and ^{224}Ra .

Actinium [1]

Experiment 13.6. SEPARATION

OF ^{227}Ac FROM URANIUM ORE [5, 7]

Actinium-227 is a member of the radioactive series of actinouranium. One tonne of uraninite (pitchblende) in radioactive equilibrium contains about 0.15 mg of ^{227}Ac , which corresponds to an activity of about 5.4×10^7 Bq ($\sim 1.46 \mu\text{Ci}$) per 100 g of ore. The separation of actinium from uranium ore includes the operations of concentrating it with the use of lanthanum as a carrier and more thorough purification from the decay products with the obtaining of a radiochemically pure preparation.

First uranyl nitrate is extracted with diethyl ether from a nitric acid solution. Next a surplus of an alkali is used to precipitate $\text{La}(\text{OH})_3$ from an aqueous solution, leaving Li, Ca, Al, and SiO_2 in the solution. The precipitate is dissolved in hydrochloric acid and purified from iron by extraction with diethyl ether, and then lanthanum is precipitated in the form of a carbonate.

The actinium concentrate obtained in this way contains radioactive impurities: Th, Po, Bi, Tl and Pb. They are separated by using extraction from hydrochloric acid solutions with a benzene solution of thenoyltrifluoroacetone. At $\text{pH} = 1$, thorium and bismuth are extracted, while at $\text{pH} = 5-5.5$ actinium with a certain amount of lead passes into the organic phase. The lead is separated by precipitation of its sulphide after reextraction from the organic phase.

The quantitative analysis of actinium is often performed according to ^{223}Fr that emits readily registered β -rays.

Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window counter. An analytical balance. Beakers for 1 litre, 500, 100, and 50 ml. A glass filter. A standard sectional funnel for filtration. Separatory funnels for 500 ml (3) and 200 ml (1).

Radioactive Substances. Uranium ore (200 g for one experiment).

Reagents. Solutions: concentrated HNO_3 , concentrated, dilute (1 : 1), and 0.1 N HCl , concentrated NH_4OH ; 40 and 1% NaOH ; saturated and 1% Na_2CO_3 ; 0.025 M thenoyltrifluoroacetone (TTA) in benzene; saturated of phosphotungstic acid. Diethyl ether saturated with a 1 N solution of HNO_3 . Diethyl ether saturated with a 6 M solution of HCl . PbCl_2 . LiNO_3 . $\text{La}(\text{NO}_3)_3$.

Performance of Work

Heat a weighed portion (200 g) of uranium ore in a beaker with 100-150 ml of concentrated nitric acid containing 2-3% of HCl almost to boiling. Filter off the insoluble residue on the glass filter (better with suction) and treat it again with nitric acid. Repeat this operation 4-5 times, the last two with the use of dilute (1 : 1) nitric acid. Collect the filtrates in the one-litre beaker, add 2 g of $\text{La}(\text{NO}_3)_3$ to them, and neutralize the surplus nitric acid with NH_4OH up to 1 N with respect to the HNO_3 . Add to this solution 10 g of LiNO_3 and extract the $\text{UO}_2(\text{NO}_3)_2$ with diethyl ether. Since the total volume of the aqueous solution is 700-800 ml, it is

good to perform extraction from aliquot parts of the solution (each part containing 150-200 ml) with equal volumes of ether saturated with a 1 *N* solution of HNO_3 . Perform the extraction until colouring of the ether layer stops.

Boil the aqueous solution to remove the ether, and add to it a 40% solution of NaOH up to a strongly alkaline reaction. Filter off the precipitate, wash it with a 1% solution of NaOH and dissolve it in 50 ml of concentrated hydrochloric acid. Bring up the acidity of the solution to 6 *M* relative to HCl and extract the FeCl_3 with an equal volume of diethyl ether saturated with 6 *M* hydrochloric acid. Remove the ether from the aqueous phase by boiling and then precipitate $\text{La}_2(\text{CO}_3)_3$ by adding a saturated solution of Na_2CO_3 . Wash the precipitate with a 1% solution of Na_2CO_3 and dissolve it in 50 ml of dilute (1 : 1) hydrochloric acid. If the precipitate is coloured, precipitate it.

Dilute the hydrochloric acid solution containing La , Ac and other decay products to 0.1 *N* with respect to HCl and transfer it into a separatory funnel with a double volume of a 0.25 *M* solution of thenoyltrifluoroacetone (TTA) in benzene. Shake the mixture for several minutes.

After separation of the layers, pour off the aqueous phase into a beaker and add NaOH until the pH is 5-5.5 according to a pH-meter. Next extract the ^{227}Ac with a new portion of the TTA solution in benzene and reextract it from the organic phase with a half volume of 0.1 *N* HCl . After separating the organic phase, add 10 mg of PbCl_2 to the aqueous solution and pass a stream of H_2S through the solution. Filter off the precipitate of PbS , and boil the filtrate to remove the surplus of H_2S . Precipitate lanthanum hydroxide $\text{La}(\text{OH})_3$ containing radiochemically pure ^{227}Ac from this solution with NH_4OH .

Use the precipitate for performing Experiments 13.7 and 13.8.

In the quantitative determination of ^{227}Ac , keep the precipitate of $\text{La}(\text{OH})_3$ containing actinium during 3.5 h to achieve equilibrium with the daughter isotope ^{223}Fr and dissolve in 10 ml of 12 *M* hydrochloric acid. Add to the solution 2-3 drops of a saturated solution of phosphotungstic acid. Filter off the precipitate on a standard sectional funnel, dry it, and measure its activity in the end-window counter.

Calculate the content of ^{227}Ac in the uranium ore.

**Experiment 13.7. SEPARATION OF $^{228}\text{Ac}(\text{MsTh}_2)$
FROM $^{228}\text{Ra}(\text{MsTh}_1)$ [8]**

The isotope ^{228}Ac is contained in old thorium preparations because it is a member of the radioactive series of thorium. Its content in equilibrium with 1 g of Th is 5×10^{-14} g, which corresponds to an activity of 1.85×10^7 Bq ($\sim 5 \mu\text{Ci}$) of ^{228}Ac per 100 g of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$.

To separate ^{228}Ac from old thorium salts, first ^{228}Ra , which is a constant source of ^{228}Ac , is separated with Ba^{2+} as a carrier. The actinium can be separated from the radium by the methods considered in this experiment. In one of them, $\text{Ba}(\text{Ra})\text{Br}_2$ is precipitated from a methanol solution by adding diethyl ether. The actinium remains in the solution. The main mass of the thorium is removed by extraction with tributyl phosphate. Then the actinium is separated from the other decay products in an ion-exchange column with the cation exchanger Dowex-50; a solution of ammonium lactate is used as the eluent.

Lately the method of chromatography on paper impregnated with inorganic ion exchangers such as zirconium phosphate or tungstate has been proposed for separating microamounts of actinium and radium.

A. COPRECIPITATION METHOD

Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window counter. An analytical balance. A platinum bowl with a capacity of ~ 100 ml. Beakers for 50 ml and 2 litres. A test tube for 3 ml with a ground-glass stopper. A glass filter. A bowl for measuring activity.

Radioactive Substances. $\text{Th}(\text{NO}_3)_4$ (an old preparation, 100 g for one experiment).

Reagents. BaBr_2 . Methanol acidified to 0.1 *N* relative to HBr . Diethyl ether. A mixture of ethanol and diethyl ether (1 : 2). Solutions: NH_4OH without CO_2 ; saturated BaBr_2 in methanol (0.1 *N* relative to HBr).

Performance of Work

Dissolve 100 g of $\text{Th}(\text{NO}_3)_4$ in one litre of water, add 20 mg of BaBr_2 (a carrier for ^{228}Ra) to the solution, and precipitate $\text{Th}(\text{OH})_4$, adding NH_4OH without CO_2 . Filter off the precipitate, evaporate the filtrate until dry, and roast

it in the platinum bowl for removing the ammonium salts. Dissolve the precipitate in 2 ml of CH_3OH acidified to 0.1 *N* relative to HBr . To this solution containing ^{228}Ra - ^{228}Ac add 20 ml of a saturated solution of BaBr_2 in methanol (0.1 *N* relative to HBr). Put 0.3 ml of the solution into the 3-ml test tube with the ground-glass stopper and add 1.8 ml of diethyl ether. Filter off the precipitate of Ba(Ra)Br_2 , wash it with 0.1 ml of a mixture of ethanol and diethyl ether (1 : 2). Combine the filtrate and the washing liquid. The ether solution contains ^{228}Ac that may be contaminated with an admixture of $^{228}\text{Th(RdTh)}$. To separate this admixture, add 1-2 drops of a saturated solution of BaBr_2 in methanol to the ether solution, and then separate the ether solution from the precipitate of BaBr_2 . Evaporate the solution containing ^{228}Ac until dry, dissolve the precipitate in a small amount of dilute acid, and transfer it into the measuring bowl or onto a standard filter for measuring β -activity.

B. ION-EXCHANGE METHOD

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. A balance. A water bath. Chromatographic columns with a height of 20 and 8 cm and a diameter of 1 and 0.3 cm, respectively. Beakers for 200 and 100 ml. A separatory funnel for 250 ml. A porcelain bowl for 200 ml. Bowls for measuring activity.

Radioactive Substances. Thorium nitrate $\text{Th(NO}_3)_4$ (an old preparation, 50 g for one experiment).

Reagents. Cation exchanger Dowex-50 $\times$ 8 (grain size 60-80 mesh) and 50 $\times$ 12 (400 mesh) in the NH_4^+ form. Solutions of 8 *M*, 3 *M*, and 0.05 *N* HCl ; 0.5, 0.65, and 0.7 *M* ammonium lactate, 40% tributyl phosphate in benzene. Benzene.

Performance of Work

First separate ^{228}Ra without a carrier from the old thorium salts. For this purpose, dissolve 50 g of $\text{Th(NO}_3)_4$ in 100 ml of 8 *M* nitric acid. Extract the main mass of the Th three times with 100-ml portions of a 40% solution of TBP in benzene during 5 min. After the third extraction, wash the aqueous phase twice with benzene and evaporate until dry on the water bath. Dissolve the dry residue in 70 ml of an 0.5 *M* solution of ammonium lactate and pass it through the chromatographic column 1 cm in diameter and 20 cm

long with the resin Dowex-50 $\times$ 8 (grain size 60-80 mesh) in the NH_4^+ form. (For how to prepare columns for work see Experiment 3.1a, Vol. 1.) Next wash the column with 50 ml of a 0.7 *M* solution of ammonium lactate to remove the rare-earth elements. Wash out the radium-228 from the column with 40 ml of a 3 *M* solution of nitric acid, evaporate the solution on the water bath, and dissolve the residue in 0.5 ml of 0.05 *N* hydrochloric acid. The solution contains ^{228}Ra without a carrier. Pass it through the column with a diameter of 0.3 cm and a length of 8 cm with the resin Dowex-50 $\times$ 12 (grain size 400 mesh) in the NH_4^+ form. To separate the ^{228}Ac , pass a 0.65 *M* solution of ammonium lactate through the column. The first 40 drops of the eluate contain ThB and ThC, and then about 60 following drops wash out all the Ac. During elution, collect 5 drops of the eluate in each of the measuring bowls, evaporate the solutions until dry, and measure the β -activity of the preparations in the end-window counter.

Plot a chromatogram by laying off the numbers of the preparations along the axis of abscissas, and their activity along the axis of ordinates.

C. PAPER CHROMATOGRAPHY METHOD

Equipment and Reagents

Equipment. A counter with a detector of β -radiation. An arrangement for chromatographing (see Fig. 3.10, Vol. 1). A thermostat. Chromatographic paper.

Radioactive Substances. A solution containing ^{228}Ra and ^{228}Ac (see Secs. A and B of this experiment).

Reagents. Solutions: 0.5 *M* NH_4Cl ; 30% ZrOCl_2 ; 60% H_3PO_4 ; 4*N* and 2 *N* HCl .

Performance of Work

Impregnate strips of chromatographic paper 6 $\times$ 40 cm in size (Whatman No. 1) as uniformly as possible with a 30% solution of ZrOCl_2 in 4 *N* hydrochloric acid and quickly put them for 5 min on pieces of filter paper to remove the surplus liquid. Next dry the strips at room temperature by putting them on another layer of filter paper. Immerse the dry strips for 2 min in a 60% solution of H_3PO_4 in 4 *N* hydrochloric acid and dry them at room temperature. In six

hours, remove the surplus H_3PO_4 from the strips by washing them with 2 *N* hydrochloric acid during 10 min, and then wash them twice in water. To increase the exchange capacity of the zirconium phosphate, additionally treat the chromatographic paper with the same 60% solution of H_3PO_4 in 4 *N* hydrochloric acid, after which put the strips during 75 min in a drying cupboard at 50 °C. Next wash them with 2 *N* hydrochloric acid, water, and dry in the air.

Apply about 0.3 ml of an aqueous solution containing ^{228}Ra - ^{228}Ac (how to prepare it is described in Secs. A and B of this experiment) to the starting line of a paper strip 2 cm wide and 12 cm long impregnated with zirconium phosphate. Put the strip into the chamber for chromatography by the ascending method (see Fig. 3.10, Vol. 1) with a small amount of water poured onto its bottom. Use a 0.5 *M* solution of NH_4Cl as the eluting solution. Heat the chamber in the thermostat to 60 °C. In these conditions, the duration of the experiment is 30 min. Register the results of chromatographing by measuring the β -activity along the paper strip (as it moves along in the counter).

Plot the activity against the distance from the starting spot. Determine the ratio of the rates of migration of radium and actinium along the chromatogram and compare it with published data (R_f).

Francium [9-10]

Experiment 13.8. SEPARATION

OF ^{223}Fr FROM ^{227}Ac [9-13]

When working with francium, one most often has to do with its most long-lived isotope $^{223}\text{Fr}(\text{AcK})$ with a half-life of 21 min. It is a decay product of ^{227}Ac , but only 1.2% of the decays of ^{227}Ac follow the scheme $^{227}\text{Ac} \rightarrow ^{223}\text{Fr} + ^4\text{He}$, so that only 12×10^3 MBq of ^{223}Fr will be in equilibrium with 1 MBq of ^{227}Ac .

The object of the present experiment is acquaintance with some ways of separating francium from actinium and the products of its decay. One of the most developed ways of separating francium and actinium is the coprecipitation of the francium with silicotungstic acid. After dissolving of the precipitate, francium can readily be separated on a cation exchanger. Another way of separating francium is

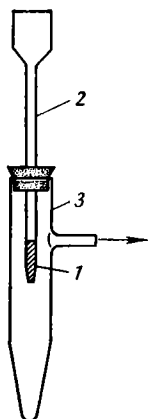


Fig. 13.2. Chromatographic column for separating francium-223: 1—cation exchanger KU-2; 2—column; 3—centrifuge test tube with side arm to vacuum pump

based on the precipitation of actinium and the products of its decay with the relevant carriers. Francium in this case remains in the solution.

The methods of paper chromatography and extraction, as is generally known, make it possible to separate elements very rapidly, and for this reason are especially valuable when working with a short-lived isotope such as ^{223}Fr .

All operations with francium must be performed as fast as possible because ^{223}Fr has a half-life of only 21 min.

A. SILICOTUNGSTIC ACID METHOD

Equipment and Reagents

Equipment and Utensils. A counter with a device for the continuous registration of the β -activity of the eluate emerging from a chromatographic column. A centrifuge. A chromatographic column 1 mm in diameter and 20 mm long (Fig. 13.2) complete with a test tube for 15 ml provided with a side arm. A beaker for 20 ml. A pipette with a syringe for 1 ml.

Radioactive Substances. Preparation of $\text{La}(\text{OH})_3$ containing $\sim 3.7 \times 10^4$ MBq of ^{227}Ac (prepared according to the procedure described in Experiment 13.6).

Reagents. Cation exchanger KU-1 (grain size 50-100 mesh) in the NH_4^+ -form. Solutions: concentrated HCl ; 0.4 M silicotungstic acid in a dropper with a pipette; concentrated HCl saturated with hydrogen chloride. Water — bidistillate.

Performance of Work

Dissolve a weighed sample of $\text{La}(\text{OH})_3$ containing ^{227}Ac in 10 ml of concentrated hydrochloric acid, and add 3-4 drops of 0.4 *M* silicotungstic acid to the obtained solution. Cool the beaker in which precipitation is being performed outside with icy water. Separate the precipitate by centrifuging, decant the liquid, and wash the precipitate twice with 10 ml of concentrated hydrochloric acid saturated with HCl. After centrifuging the precipitate and decanting the hydrochloric acid, remove the remaining acid from the centrifuge test tube with the aid of the pipette. Dissolve the precipitate in 1 ml of bidistilled water. Pass the solution through a column with a cation exchanger (see Fig. 13.2) thoroughly washed with bidistilled water. The rate of passing the solution through the column in elution must be 0.5 ml/min. Next wash the column with bidistillate at the same rate (1-2 ml), transfer the solution into the second test tube with the side arm and rapidly (during 2-3 min) wash it with 0.5 ml of concentrated hydrochloric acid. A solution containing ^{223}Fr without a carrier in the radiochemically pure state is collected in the test tube.

The solution is used for performing Experiments 13.11-13.14.

B. COPRECIPITATION METHOD

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. Beakers for 50 ml (3). Funnels for filtration (2). A bowl for evaporation.

Radioactive Substances. A preparation of $\text{La}(\text{OH})_3$ containing ^{227}Ac (obtained as described in Experiment 13.6).

Reagents. Na_2CO_3 , LaCl_3 , $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. Solutions: 0.01 *M* K_2CrO_4 ; NH_4OH (1 : 1); concentrated HCl.

Performance of Work

Add a surplus of Na_2CO_3 to 10 ml of a hydrochloric acid solution containing ^{227}Ac (with La as a carrier) and boil the mixture. Filter off the precipitate containing decay products of actinium: ^{223}Ra (AcX), ^{227}Th (RdAc), ^{211}Pb (AcB), and ^{211}Bi (AcC), acidify the filtrate with hydrochloric acid, and boil it to remove CO_2 . Add 5 mg each of LaCl_3 and BaCl_2 to the solution after cooling and precipitate lanthanum and

barium chromates by adding to the solution a 0.1 *M* solution of K_2CrO_4 and NH_4OH (1 : 1). The precipitate contains ^{227}Th with traces of ^{227}Ac and ^{223}Ra . Filter it off, evaporate the filtrate containing radiochemically pure ^{223}Fr , and use it for measuring the activity.

Identify the ^{223}Fr according to its half-life.

C. PAPER CHROMATOGRAPHY METHOD

A variant of the paper chromatography method is used that makes it possible to separate francium and actinium very rapidly. A high rate of separation is achieved because short strips of paper are used for chromatographing, while the separation itself is performed in a device placed in a thermostat, which makes it possible to maintain an increased temperature of the experiment.

Equipment and Reagents

Equipment. A counter with a detector of β -radiation. A device for chromatographing (see Fig. 3.10, Vol. 1). A thermostat.

Radioactive Substances. A solution containing $\sim 3.7 \times 10^4$ Bq ($\sim 1 \mu Ci$) of ^{227}Ac (obtained following the procedure in Experiment 13.6).

Reagents. A 10% solution of $(NH_4)_2CO_3$.

Performance of Work

Concentrate the solution containing ^{227}Ac to a small volume and transfer it onto the edge of a paper strip (2×12 cm). In two or three hours (when equilibrium sets in between the ^{227}Ac and ^{223}Fr), place the chromatogram into the device (see Experiment 13.7) and lower its end near which the starting line is into a 10% solution of $(NH_4)_2CO_3$. Maintain the temperature in the device at about $60^\circ C$ with the aid of the thermostat. The chromatographing continues from 6 to 15 min.

Scan the dried chromatogram (consecutively measure the activity of the separate parts of the chromatogram) in the end-window counter for revealing the section containing ^{223}Fr . The actinium and the products of its decay remain at the spot of application of the initial solution on the chromatogram.

D. EXTRACTION METHOD

In the present experiment, francium is separated from actinium by extracting the ^{223}Fr in the form of its tetraphenyl borate with nitrobenzene from an aqueous solution at $\text{pH} = 9$. The radium-223 is bound by Na-EDTA.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation, A separatory funnel for 25 ml. Beakers for 50 ml (2).

Radioactive Substances. A preparation of $\text{La}(\text{OH})_3$ containing ^{227}Ac (its preparation is described in Experiment 13.6).

Reagents. Sodium tetraphenyl borate. Na-EDTA. Nitrobenzene. Solutions: 1 *N* HCl; 10% $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$.

Performance of Work

Dissolve a preparation of $\text{La}(\text{OH})_3$ containing ^{227}Ac in 0.5 ml of 1 *N* hydrochloric acid, add to the solution $\text{Na}_2\text{B}_4\text{O}_7 \times 10\text{H}_2\text{O}$ to a pH of 9 and sodium tetraphenyl borate so as to obtain a 0.05 *M* solution of it. The volume of the solution must not exceed 1 ml. To combine the ^{223}Ra , add Na-EDTA (EDTA) to a concentration of 1%. Extract the ^{223}Fr from the solution with an equal volume of nitrobenzene during 3 min. After separation of the aqueous phase, reextract the francium from the nitrobenzene with a double volume of 1 *N* hydrochloric acid.

Identify the ^{223}Fr according to its half-life.

Experiment 13.9. REACTIONS

OF COPRECIPITATION OF Fr [9, 11, 14, 15]

Here we perform experiments that make it possible to identify the separated francium, confirm its nature as the most active alkali metal, and separate it without a carrier.

A. DETERMINING THE DEGREE OF PURITY OF Fr

When preparations of ^{223}Fr are obtained, it may be contaminated with a number of radioactive admixtures (radium, actinium, radioactive isotopes of lead—ThB and RaD, protactinium). The purity of Fr is monitored by consecutively precipitating BaCO_3 , $\text{La}(\text{OH})_3$, PbS, and MnO_2 from the solution containing it. Francium does not coprecipitate

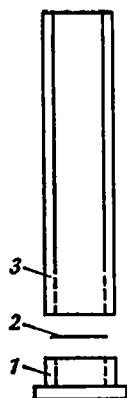


Fig. 13.3. A centrifuge Plexiglas tube with a screwing off bottom:

1—threaded bottom; 2—disk-substrate for gathering precipitate; 3—threaded cylinder

with any of the precipitates listed above. The admixture of radium coprecipitates with BaCO_3 , actinium with $\text{La}(\text{OH})_3$, the lead isotopes with PbS , and, finally, the protactinium with MnO_2 . By monitoring the coprecipitation of these elements, one can determine the degree of purity of ^{223}Fr .

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. A centrifuge. A lamp for evaporation. Transparent thermoplastic (Plexiglas) test tubes for centrifuging with a screwing off bottom and a set of disk substrates to them made from aluminium, a fluoroplastic, or mica (Fig. 13.3). Pipettes for 0.1 ml (5) and for 1 ml (1).

Radioactive Substances. A solution containing the chloride of ^{223}Fr with an activity of $\sim 10^4$ cpm.

Reagents. Hydrogen sulphide water. Solutions: BaCl_2 , LaCl_3 , MnSO_4 , KMnO_4 , and $\text{Pb}(\text{NO}_3)_2$ (each with a concentration of 10 mg/ml); 1 M Na_2CO_3 and NH_4OH .

Performance of Work

Introduce 1 ml of a solution of BaCl_2 , LaCl_3 , MnSO_4 , or $\text{Pb}(\text{NO}_3)_2$ into each of four Plexiglas tubes (see Fig. 13.3) with a screwing off bottom (put a disk of mica, a fluoroplastic, or aluminium foil on the bottom). Add 0.1 ml of a solution of the chloride of ^{223}Fr to each tube, and stir the mixture.

Next precipitate BaCO_3 with a solution of Na_2CO_3 , $\text{La}(\text{OH})_3$ with a solution of NH_4OH , PbS with hydrogen sulphide, and MnO_2 with a solution of KMnO_4 .

Thoroughly mix the precipitates by shaking them for 3-5 min, separate by centrifuging, and immediately measure the β -activity of an aliquot part of the centrifugate by applying it onto a substrate of mica, a fluoroplastic, or aluminium, and rapidly evaporating under a lamp. Decant the centrifugate into other tubes. Next wash the precipitates with a solution of alcohol with water, centrifuge, decant, screw off the bottom of the centrifuge tubes, and carefully extract the substrates with the precipitates. Rapidly dry the precipitates under the lamp and measure their activity.

In four hours, i.e. after complete decay of the ^{223}Fr , repeat the activity measurement of the same aliquot part of the clear solution and the precipitates.

Use the data obtained to determine the degree of purity of the ^{223}Fr used (taking into account that α -active ^{223}Ra with $T_{1/2} = 11.2$ days forms upon the decay of the ^{223}Fr).

B. DETERMINING THE DEGREE OF COPRECIPITATION OF Fr, Cs, AND Rb WITH POTASSIUM PERCHLORATE AND CESIUM CHLOROPLATINATE

A comparison of published data on the solubility of the perchlorates and chloroplatinates of the alkali metals allows the conclusion to be made that francium salts should have the lowest solubility as compared with the salts of the other alkali metals. Francium is the closest to cesium in its properties, and therefore cesium perchlorates and chloroplatinates can be used as carriers in the coprecipitation of francium. The object of this work is to confirm this conclusion in experiments involving the coprecipitation of ^{223}Fr , ^{134}Cs , and ^{86}Rb .

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. A centrifuge. A lamp for evaporation. Transparent thermoplastic (Plexiglas) test tubes (4) for centrifuging with a screwing off bottom and a set of disk substrates to them made from aluminium, a fluoroplastic, or mica (see Fig. 13.3). Pipettes with syringes for 0.1 ml (4) and for 5 ml (1).

Radioactive Substances. Solutions containing chlorides of ^{223}Fr , ^{134}Cs , and ^{86}Rb with an activity of about 10^4 cpm for each isotope.
Reagents. Ethanol. Solutions: concentrated HClO_4 , 10% KCl ; 1% H_2PtCl_6 , 1% CsCl .

Performance of Work

Introduce 0.2 ml of a KCl solution and 2 ml of ethanol into each of four centrifuge tubes. Next add 0.1 ml of a solution of the chloride of ^{223}Fr to two of the tubes (two tubes are used to run two parallel experiments whose results are averaged at the end of the work), and 0.1 ml of a solution of the chlorides of ^{134}Cs and ^{86}Rb , respectively, into each of the other two tubes. After this, use HClO_4 to precipitate KClO_4 . It is desirable to perform precipitation at a temperature of 5-10 °C. Centrifuge the precipitate, decant the clear solution, apply aliquot parts of it (0.1 ml each) to aluminium disks, and evaporate them under a lamp. Screw off the bottoms of the test tubes, extract the substrates with the precipitate, and also dry the precipitates under the lamp. Measure the activity of all the specimens obtained. Determine the degree of coprecipitation of ^{223}Fr , ^{134}Cs , and ^{86}Rb with potassium perchlorate from the ratio of the activity of the precipitate to that of the solution obtained after precipitation.

Perform the coprecipitation of ^{223}Fr , ^{134}Cs , and ^{86}Rb with Cs_2PtCl_6 in a similar way.

C. STUDYING THE COPRECIPITATION OF Fr AND Cs WITH HETEROPOLYACIDS

The coprecipitation of francium with heteropolyacids in solutions of concentrated hydrochloric acid is used for separating it without a carrier.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. A centrifuge. A lamp for evaporation. Transparent thermoplastic (Plexiglas) tubes (4) for centrifuging with a screwing off bottom and a set of disk substrates to them made from aluminium, a fluoroplastic, or mica (see Fig. 13.3). Pipettes with syringes for 0.1 ml (4) and for 5 ml (1).

Radioactive Substances. Solutions of chlorides of ^{223}Fr and ^{134}Cs with an activity of $\sim 10^4$ cpm for each isotope.

Reagents. Solutions: concentrated HCl ; 0.5 M silico- and phosphotungstic, silico- and phosphomolybdic acids.

Performance of Work

Introduce 2 ml of concentrated hydrochloric acid, and then add 0.1 ml of a solution of the chloride of ^{134}Cs into each of four centrifuge tubes. Add 0.1 ml of one of the 0.5 *M* solutions of the heteropolyacids (silico- and phosphotungstic, silico- and phosphomolybdic) to each of the solutions. Thoroughly stir the precipitates and centrifuge them. Apply 0.1 ml of the clear solution onto each disk and rapidly evaporate it under the lamp. Decant the remaining part of the clear solution, wash the precipitates with alcohol, extract them from the tubes, and dry them. Measure the activity of all the specimens.

Run similar experiments involving the coprecipitation of ^{223}Fr with the same polyacids. Calculate the degree of coprecipitation of cesium and francium with the heteropolyacids as described in Sec. B of this experiment.

Experiment 13.10. INVESTIGATING THE VOLATILITY OF FrCl [10, 11, 15]

Francium halides, like the halides of the other alkali metals, have an appreciable volatility at temperatures above 300 °C. It is general knowledge that the volatility of the chlorides increases in the alkali metal series from potassium to cesium and, consequently, we can presume that the volatility of francium chloride will be greater than that of the other alkali metal chlorides. The object of the present experiment is to verify the correctness of this conclusion.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. Crucible furnaces (3). Thermocouples with a galvanometer for determining the temperature within the interval from 600 to 1000 °C. Long pincers. Platinum or quartz disks 15 mm in diameter. A lamp for evaporation.

Radioactive Substances. A solution containing the chloride of ^{223}Fr with an activity of 10^4 cpm. A solution containing ^{137}Cs without a carrier.

Performance of Work

Apply 0.1 ml of a solution containing ^{223}Fr with a micropipette onto each of four platinum or quartz disks. Rapidly evaporate the solutions under the lamp. Use one of the solu-

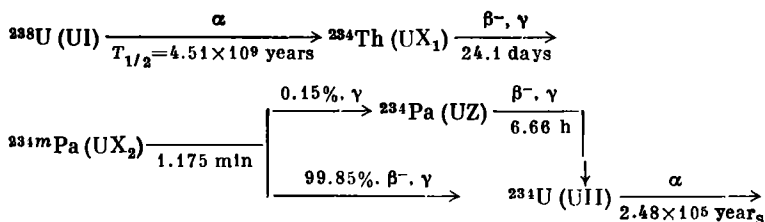
tions as a standard. Introduce the remaining preparations into the three crucible furnaces, in which temperatures of 600, 800 and 1000 °C (respectively) are maintained that are established beforehand. Heat the disks during 10 min. Next extract them from the furnaces with the pincers and cool them. Measure the activity of all four preparations. Determine the fraction of the evaporated FrCl (in %) by comparison with the standard. Plot the data in the form of graphs of the amount (in %) of evaporated francium chloride versus the temperature.

Simultaneously perform similar experiments with a solution containing radioactive cesium without a carrier. Compare the rates of evaporation of the francium and cesium chlorides.

Protactinium [16]

Experiment 13.11. SEPARATION OF SHORT-LIVED PROTACTINIUM ISOTOPE UX_2 (^{234m}Pa) FROM URANYL CHLORIDE SOLUTION

The short-lived protactinium isotope UX_2 ($T_{1/2} = 1.175$ min) is a member of the natural radioactive series of ^{238}U and forms as a result of the following nuclear transformations:



Owing to the high rate of radioactive decay of UX_2 , the methods of separating it must be sufficiently rapid. This requirement is met, particularly, by the method of extraction of UX_2 from an aqueous solution of UO_2Cl_2 with the aid of diethyl ether used in the present experiment. When performing extraction in the presence of the salting-out agent $MgCl_2$, ^{234m}Pa (in addition to ^{234}Pa) and part of the uranium pass into the organic phase; ^{234}Th (UX_1) remains completely in the aqueous phase. The physical identification of ^{234m}Pa is performed by measuring the half-life.

Equipment and Reagents

Equipment and Utensils. A counter with a scintillation detector [a crystal of NaI (Tl) with a well for measuring the activity of liquid preparations of γ -emitters]. An analytical balance. Test tubes (4) for measuring the radioactivity entering the well of the crystal. Test tubes (4) with ground-glass stoppers for 15-30 ml. A measuring cylinder for 10 ml. A pipette for 5 ml with a syringe. Beakers for 100 ml (2).

Radioactive Substance. 6 g of UO_2Cl_2 .

Reagents. MgCl_2 (anhydrous). Diethyl ether. An 8 M solution of HCl.

Performance of Work

Dissolve 6 g of UO_2Cl_2 and 5 g of MgCl_2 in 6 ml of 8 M hydrochloric acid with heating in a 100-ml beaker. After cooling, transfer the solution into a test tube for extraction. Mix 6 ml of diethyl ether with 6 ml of 8 M hydrochloric acid containing 5 g of MgCl_2 by shaking and combine this solution with the one of UO_2Cl_2 .

Shake the mixture during 15 s. Upon extraction, two ether layers and one water layer form. Take a sample with a volume of 2-3 ml from the upper ether layer with the pipette and syringe for measuring its activity and transfer it into a test tube. Immediately place the latter in the well of the counter and begin to measure the activity. Do this during five minutes, from 10 to 20 s at a time after every 5 s. When plotting a graph, relate the measurement results to the middle of the measuring time interval. Find the volume of the upper ether layer.

Repeat the extraction of ^{234m}Pa two or three times with ether from the same aqueous solution and the measurement of the activity of the upper ether layer and its volume. Depict the measurement results graphically in coordinates of the logarithm of the activity against the time from the instant of layer separation and find the half-life of the isotope contained in each extract. Calculate the mean value, determine its error, and compare the result with a tabulated value. Using the obtained graph, find the activity of the ^{234m}Pa corresponding to the instant of phase separation. Taking into account the ratio of the volumes of the measured sample and of the entire upper ether layer, and also the value of the counter's registration coefficient, determine the absolute activity of the separated ^{234m}Pa and then calculate the extraction of the ^{234m}Pa (in % with respect to the equilibrium value).

We must stress that all the experimental work must be performed quickly so that by the beginning of measurement the registered activity would be at least 5 cps.

Experiment 13.12. SEPARATION OF PROTACTINIUM ISOTOPE UZ (^{234}Pa) FROM SOLUTION CONTAINING UX_1

The γ -decay (0.15 %) of UX_2 (see the decay diagram, p. 167) results in the formation of the relatively long-lived protactinium isotope UZ (^{234}Pa) whose half-life is 6.66 h. Sometimes, UZ may be useful as a radioactive tracer of protactinium. The methods of its separation are naturally absolutely the same as those of separating UX_2 . Particularly, both nuclear isomers of ^{234}Pa can be separated in accordance with the procedure described in the preceding experiment. Since ^{234}Pa decays comparatively slowly, a procedure based on the precipitation of fluorides can be used for its separation. Although this procedure is not as rapid as the extraction one, it ensures a higher separation of the Pa from the parent UX_1 . In the present experiment, the precipitation of fluorides in dilute hydrofluoric acid is used for the separation of UZ (together with rapidly decaying UX_2) from solutions containing ^{234}Th (UX_1). In these conditions, protactinium and tantalum fluorides are soluble quite well, while thorium fluoride is virtually insoluble.

Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window or 4π counter. A centrifuge. An analytical balance. A lamp for evaporation. An organic glass test tube for centrifuging (see Fig. 13.3) with substrates made from polytetrafluoroethylene (Teflon) or metallic tantalum. Glass test tubes for centrifuging for 10 ml (4). Chemical beakers for 100 (1) and 50 ml (2). A funnel for filtration. A measuring cylinder for 10 ml. A glass rod. Paraffin-coated beakers for 100 ml (2), a funnel and a rod. (Instead of the paraffin-coated glass utensils, it is convenient to use utensils made from Teflon, polyethylene, organic glass, etc., suitable for work with hydrofluoric acid.)

[Radioactive Substances. UX_1 prepared according to the description in Experiment 12.11. 60 mg of $\text{Th}(\text{NO}_3)_4$ (or an equivalent amount of the crystal hydrate of this salt)

Reagents. Ta_2O_5 . BaCl_2 . $\text{Pb}(\text{NO}_3)_2$. Solutions: concentrated H_2F_2 and ammonia; 2 N HCl, 0.2 N H_2SO_4 . Ethanol. Ether.

Performance of Work

Separate UX_1 according to the procedure described in Experiment 12.11. Use a nitrate solution containing 10-12 g of $UO_2(NO_3)_2 \cdot 6H_2O$ as the initial one. Decompose the oxalic acid in the solution obtained by evaporating it until dry in the presence of 10 ml of nitric acid and 10 ml of hydrogen peroxide. Wash off the dry residue after decomposition with 10 ml of 2 *N* hydrochloric acid, and transfer the solution into a paraffin-coated beaker.

Dissolve 20 mg of $Th(NO_3)_4$ in 10 ml of distilled water in a 50-ml beaker. Precipitate barium and lead sulphates from the solution to remove the radioactive decay products of ^{232}Th . For this purpose, introduce 10 mg each of $BaCl_2$ and $Pb(NO_3)_2$ into the solution, and after their dissolving add 2 ml of 0.2 *N* sulphuric acid to the solution dropwise with thorough mixing. Separate the barium and lead sulphates that precipitate by centrifuging. See what members of the radioactive series of ^{232}Th are removed here.

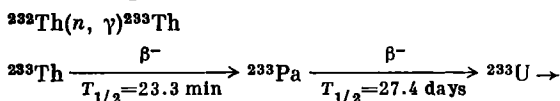
Transfer the thorium nitrate solution into the paraffin-coated beaker containing UX_1 . Slowly add to it with constant stirring of the liquid 10 ml of a concentrated solution of H_2F_2 in which 25 mg of Ta_2O_5 were preliminarily dissolved. After the precipitation of ThF_4 , centrifuge the liquid from the beaker in two or three portions (perform each centrifuging 3-5 min at 3000 rpm). Pour all the portions of the solution separated from the ThF_4 into a paraffin-coated beaker. Repeat the precipitation of the ThF_4 , using a new portion of the solution of $Th(NO_3)_4$ purified of the decay products. Do not add Ta_2O_5 to the H_2F_2 solution upon the repeated precipitation of the ThF_4 . Transfer the solution obtained after the final separation of the ThF_4 into the 100-ml beaker and precipitate tantalum hydroxide by adding a concentrated solution of ammonia to it dropwise. Let the precipitate settle, and pour off the main part of the clarified solution (the volume of the liquid remaining in the beaker must not exceed 10 ml). Make the precipitate turbid and transfer the suspension into a centrifuge tube with a screwing off bottom (see Fig. 13.3). Centrifuge the precipitate 3-5 min at 3000 rpm, pour off the clear solution into the waste vessel, and wash the precipitate with water, alcohol, and ether, after which screw off the bottom of the tube and carefully extract the substrate with the precipitate. Coat the

precipitate with varnish and rapidly dry it under a lamp.

Identify the isotope contained in the preparation according to its half-life (measurement of the activity may be begun in 25-30 min after the final precipitation of the ThF_4 ; during this time the UX_2 will decay completely). Appraise the registration coefficient and determine the yield of the UZ (as a percentage of the equilibrium content of UZ in the sample of uranyl nitrate used).

Experiment 13.13. SEPARATION OF ^{233}Pa FROM IRRADIATED Th [17-19]

As a result of the rapid β -decay of ^{233}Th appearing when the natural isotope ^{233}Th is irradiated by slow neutrons, the β -radioactive isotope ^{233}Pa forms:



^{233}Pa is a convenient tracer in the radiochemical and analytical investigations of protactinium (the energy $F_{\max}$ of the β -particles of ^{233}Pa equals 0.14, 0.26, and 0.57 MeV).

Protactinium can be separated from the parent thorium with a high degree of separation by both the ion-exchange and the extraction methods.

A. PREPARATION OF THORIUM NITRATE SPECIMENS FOR IRRADIATION BY NEUTRONS

When thorium nitrate specimens are handed over for irradiation by a flux of neutrons of an atomic reactor, the general rules must be followed. The thorium salt [usually the crystal hydrate having the composition $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ is used] is sealed in a vacuum (1.33 Pa) in a small quartz ampoule that is thoroughly wiped outside with a wad wetted in benzene (for removing traces of fat) and is then placed in a special block made from highly pure aluminium. The substance used for irradiation must be chemically pure. Proceeding from the value of the neutron flux intensity in the reactor (10^{11} - 10^{13} cps/cm²) and assuming that the effective cross section of neutron capture by ^{232}Th is 7.5 barn, one calculates the duration of irradiation after which the

portion of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ with a mass of 10 mg acquires an activity of 370 MBq (10 μCi).

The crystal hydrate $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ readily melts. This is attended by its partial decomposition with the evolution of nitrogen oxides. The result is an increase in the pressure in the ampoule, which may cause it to explode. This is why a sealed quartz ampoule with the substance must be tested by keeping it for 8-10 hours in boiling water.

The lead container with the aluminium block obtained after irradiation is left to "cool" during a week (during this time the short-lived isotopes of aluminium, silicon, etc. completely decay). Next a special device is used to open the block, extract the quartz ampoule from it, and the separation of protactinium is begun. When performing this work, especially when opening the block and extracting the ampoule, the experimenter must use a dosimetric instrument to see that the dose he receives does not exceed the permissible value.

B. ION-EXCHANGE SEPARATION OF ^{233}Pa

The method is based on the circumstance that in concentrated hydrochloric acid solutions, protactinium forms a negatively charged chloride complex reacting with the anion exchanger, while the thorium remains in the cation form.

Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window counter. A chromatographic column with an internal diameter of 5 mm and a length of 10-12 cm combined with a radiometric instrument making it possible to continuously measure the activity of the solution emerging from the column. Chemical beakers for 100 (1) and 50 ml (2). Measuring cylinders for 10 and 25 ml. A glass bowl for measuring activity. A pipette for 2 ml with a syringe.

Radioactive Substances. A specimen of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ irradiated by neutrons and having a specific activity of about 10^7 Bq/g and a mass of 10 mg.

Reagents. Anion exchanger Dowex 1×2 or 1×4 (with a grain size of 200-400 mesh). 4 and 8 M solutions of HCl with a purity not below the grade "pure for analysis".

Performance of Work

Following the procedure set out in Experiment 12.11, transfer the previously prepared anion exchanger into the chromatographic column. See that there are no air bubbles

in the resin layer. Pour 8 *M* hydrochloric acid into the column.

In a shielding sealed chamber for work with β -radioactive isotopes, open the quartz ampoule (you may carefully break off the tip of the ampoule with pliers), and dissolve the irradiated thorium nitrate in 6 ml of 8 *M* hydrochloric acid. According to the readings of the dosimetric instrument, see that the shielding used ensures the lowering of the obtained dose to permissible values. If necessary, increase the shielding.

Pass the thorium nitrate solution through the column at a rate of 0.2-0.3 ml/min. The thorium passes into the filtrate, while the protactinium is retained on the resin. For complete removal of the thorium, wash the column three times with 8 *M* hydrochloric acid in 10-ml portions, after which eluate the protactinium with 4 *M* hydrochloric acid. The rate of flow of the washing solution (8 *M* hydrochloric acid) should be 1 ml/min, and of the eluting one (4 *M*)—0.5 ml/min. The termination of washing out of the ^{233}Pa is determined according to the readings of the radiometric instrument.

Transfer an aliquot portion of the solution of ^{233}Pa into the glass bowl and prepare the substance for activity measurement by evaporation. On the basis of the value of the registration coefficient of the radiometric apparatus used, and also taking into account the total volume of the obtained solution and the activity of its aliquot portion, find the absolute activity of the separated ^{233}Pa and appraise the fraction of the isotope extracted (in % of the theoretical yield). The isotope can be identified according to the results of determining its half-life. Perform the measurements during a month. Monitor the stability of functioning of the counting installation during this time with the aid of a uranium preparation.

C. EXTRACTION SEPARATION OF ^{233}Pa

^{233}Pa can be separated rapidly and completely (up to 99.7% from the parent thorium with the aid of chloroform solutions of *N*-benzoylphenylhydroxylamine (*N*-BPHA)— $\text{C}_6\text{H}_5\text{CON}(\text{OH})\text{C}_6\text{H}_5$ or neocupferron (*N*-nitrosonaphthylhydroxylamine)— $\text{C}_{10}\text{H}_7\text{N}(\text{OH})\text{NO}$. When these reagents are

used, the protactinium is extracted into the organic phase virtually completely, while the thorium remains in the aqueous phase.

Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window counter. A separatory funnel for 50 ml. Chemical beakers for 50 (1) and 100 ml (1). A measuring cylinder for 10 ml. A pipette for 2 ml with a syringe. A polytetrafluoroethylene (Teflon) and a glass bowl for measuring activity (1 of each).

Radioactive Substances. A specimen of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ irradiated by neutrons, having a specific activity of about 10^7 Bq/g and a mass of about 10 mg.

Reagents. Solutions: 0.1 M N-BPHA and 0.01 M neocupferron* in CHCl_3 , 3 M and 10 M HCl; 0.5 N H_2F_2 .

Performance of Work

Prepare a solution of irradiated thorium nitrate in 10 ml of 3 M hydrochloric acid (see Sec. B of this experiment) in a shielding sealed chamber for work with β -radioactive isotopes with constant dosimetric control. Transfer the solution into the 50-ml separatory funnel, add 5 ml of an 0.1 M solution of N-BPHA in CHCl_3 (or the same volume of a 0.01 M solution of neocupferron) to it and perform extraction by vigorously shaking the separatory funnel during 10 min (*perform shaking without fail behind the protective screen over a tray*).

Let the liquid settle, and then separate the organic phase containing the ^{233}Pa . Reextract the protactinium from it with two 10-ml portions of 0.5 N hydrofluoric acid (if N-BPHA was used for extraction), or with the same volume of a 10 M solution of HCl (when neocupferron was used as the extracting agent). Reextraction with the aid of 0.5 N hydrofluoric acid may be performed in a conventional 50-ml glass separatory funnel; the duration of each reextraction must not exceed 5-7 min. Transfer part of the solution containing ^{233}Pa with a pipette into the Teflon (hydrofluoric acid solution) or glass (hydrochloric acid solution) bowl and prepare the substance for activity measurement by evapora-

* The commercial neocupferron is the relevant ammonium salt.

tion. On the basis of the results of activity measurement and with a view to the total volume of the obtained solution of ^{233}Pa , find the degree of extraction of protactinium (in %) according to the ratio to the theoretical yield in a nuclear reaction. Identify the separated isotope as described in Sec. B of the present experiment.

Experiment 13.14. SEPARATION OF LONG-LIVED ISOTOPE ^{231}Pa FROM URANIUM ORE [4, 14]

Recent years have seen numerous investigations of the chemistry of protactinium with the use of macroamounts of this element. The long-lived α -radioactive isotope ^{231}Pa with a half-life of 3.24×10^4 years was used in these investigations. It is a member of the radioactive series of actinouranium (^{235}U). One tonne of uranium (the natural mixture of isotopes) in equilibrium contains about 0.32 g of protactinium, i.e. almost as much as it contains radium (0.34 g). But owing to the features of the chemical behaviour of protactinium, it is more difficult to separate it from uranium ores than radium.

The obtaining of gramme amounts of protactinium can be based, particularly, on the fact that protactinium as regards some of its properties is close to zirconium, but differs from it in a more basic nature. Protactinium can be separated and concentrated by using zirconium phosphate as a carrier. Microamounts of ^{231}Pa free of admixtures of foreign α -emitters can be comparatively rapidly extracted from uranium ores described in the present experiment with the aid of zirconium phosphate.

Equipment and Reagents

Equipment and Utensils. An ionization chamber operating in current conditions and intended for registering α -radiation. A sand bath. A balance. Measuring cylinders for 10 and 50 ml. A funnel. Chemical beakers for 100 (3) and 250 ml (1). A porcelain bowl for 100 ml. A glass rod. A nickel bowl or a nickel crucible for 20-30 ml for alkaline melting. An organic glass tube for centrifuging (see Fig. 13.3) with polytetrafluoroethylene (Teflon) or tantalum substrates.

Radioactive Substances. Uranium ore with an exactly known content of uranium.

Reagents. Na_2CO_3 , K_2CO_3 , KHSO_4 . Solutions: 1% $\text{ZrO}(\text{NO}_3)_2$; 5% H_2O_2 , 1% Na_3PO_4 ; concentrated and dilute (1 : 1) HNO_3 ; concentrated ammonia. Acetone.

Performance of Work

Transfer a portion of uranium ore containing ~ 200 mg of uranium into a 100-ml beaker, add 50 ml of concentrated nitric acid to it, and heat the mixture two hours on the sand bath, adding acid to the beaker as it boils out. Next cool the solution, pour it into the porcelain bowl, and evaporate the liquid until dry. Dissolve the separated precipitate in 30 ml of dilute (1 : 1) nitric acid. Add 2 ml of a 1% solution of $\text{ZrO}(\text{NO}_3)_2$ and 5 ml of 5% hydrogen peroxide to the solution. The presence of the peroxide is needed to keep the titanium in the solution upon the following joint precipitation of zirconium and protactinium phosphates.

The phosphates are precipitated by heating the solution to 80°C and adding 5 ml of a 1% solution of Na_3PO_4 to it. Let the precipitate coagulate, after which carefully transfer it onto a fluted filter and wash it with three 30-ml portions of a 1% solution of Na_3PO_4 .

To purify the protactinium from the contaminating α -emitters captured by the precipitate, reprecipitate the phosphate. For this purpose, preliminarily transfer the zirconium and protactinium phosphates into oxides by melting them in the nickel bowl or crucible with a mixture consisting of 0.1 g of Na_2CO_3 and 0.1 g of K_2CO_3 . Leach out the surplus of carbonates from the melt with hot water, and fuse the remaining residue with 0.1 g of KHSO_4 . Dissolve the product of fusing in 30 ml of dilute (1 : 1) nitric acid. Precipitate zirconium and protactinium hydroxides from the solution with ammonia, filter off the precipitate, and dissolve it in 30 ml of concentrated nitric acid. Perform the following operations of precipitating zirconium phosphate as described above.

Wash the precipitate obtained as a result of all the operations with acetone, dry, and weigh it. Next suspend it in 5 ml of water, and, using the tube for centrifuging with a screwing off bottom (see Fig. 13.3), prepare the substance for measuring its activity. Use the measurement results to evaluate the specific activity of the precipitate.

To convince yourself in the radiochemical purity of the obtained specimen of ^{231}Pa , perform another reprecipitation of the $\text{Zr}_3(\text{PO}_4)_4$ and compare the value of the specific activity of the phosphate found after this with that established pre-

viously. Coincidence of the specific activity values indicates that the preparation contains no foreign α -radioactive isotopes.

Use the results to calculate the content of ^{231}Pa in the initial ore and determine the degree of extraction of the isotope (in %).

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Chapter 14 The Chemistry of Neptunium [1-4]

Experiment 14.1. OXIDATION-REDUCTION REACTIONS IN SOLUTIONS [1-4]

Identification of the oxidation states and investigation of the chemical behaviour of neptunium are usually performed by methods of coprecipitation, extraction, and ion exchange when working with tracer amounts (usually ^{239}Np) or by the spectrophotometric method (when working with macroamounts of ^{237}Np). The characteristic absorption bands are presented in Table 14.1.

The radiometric methods of analysing neptunium are based on the measurement of the α -radiation of ^{237}Np and the hard β -radiation of ^{239}Np . One usually has to do with very dilute solutions, when the activity of the ^{237}Np is not high (the specific activity is 1.52×10^6 dpm/mg); the energy of the α -radiation of ^{237}Np is also low, and therefore a high degree of purification of the neptunium from the fission-product radioactive isotopes is needed. The content of ^{237}Np is also determined by the method of isotope dilution with the aid of ^{239}Np (see Chap. 17).

A. PREPARATION OF Np^{III}

Trivalent neptunium is extremely unstable to oxidation, which hinders its preparation and investigation. Sodium formaldehyde sulfoxylate (rongalite) $\text{HOCH}_2\text{S}(\text{O})\text{ONa} \times 2\text{H}_2\text{O}$ is used to reduce neptunium to the trivalent state in solutions of HNO_3 , HCl , and HClO_4 (1-2 *N*). Neptunium is reduced the most completely in an atmosphere of nitrogen under the action of a 1 *N* solution of HCl containing 20 g/litre of $\text{N}_2\text{H}_4 \cdot \text{HCl}$ and 10 g/litre of rongalite. When the solution stands in contact with the air, Np^{III} is oxidized to Np^{IV} with the passage of time.

Table 14.1. Absorption Characteristic of Neptunium Ions in Aqueous Solutions*

Oxidation state	Ion	Colour	λ , nm**	Molar absorption coefficient	λ , nm	Molar absorption coefficient
			1 N HClO ₄		1 N HNO ₃	
3	Np ³⁺	Light blue or purple	233.5***	2295	—	—
			267***	1593	—	—
			552	44.5	—	—
			602***	25.8	—	—
			664***	30.5	—	—
			787.5***	48.2	—	—
4	Np ⁴⁺	Yellow-green	—	—	420	~ 16
			504***	22.9	500	~ 15
			590.5***	16.1	~ 600	~ 7.5
			723	67.0	~ 745***	~ 3.7
			743***	43.0	—	—
			825***	24.5	800	~ 24
			964	185	975	~ 32
5	NpO ₂ ²⁺	Green	428	11.4	—	—
			617***	23.7	~ 617***	~ 18
			983	~ 293	~ 290	~ 180
6	NpO ₂ ²⁺	From pink to red	476	6.4	—	—
			557	6.8	—	—
			—	—	1230***	~ 43
7	NpO ₂ ²⁺	Bright green	410	1370****	—	—
			625	385****	—	—

* Given for neptunium in weakly complexing media.

** The most characteristic absorption bands are in bold-face type.

*** Absorption at these wavelengths obeys the Bouguer-Lambert-Beer law.

**** In solutions of 0.2-5 M relative to NaOH or KOH.

Equipment and Reagents

Equipment and Utensils. A spectrophotometer (SF-4, SF-4A, SF-8, etc.). A rectangular quartz or glass planchet with an absorbing layer 1 cm thick. Glass beakers for 10 ml (2). A capillary pipette for 2-3 ml.

Radioactive Substances. 4-5 ml of a solution containing 0.007 mol/litre of $^{237}\text{Np}^{\text{IV}}$, 1 N relative to HCl.

Reagents. A concentrated solution of HClO_4 . Rongalite. $\text{N}_2\text{H}_4 \times \text{HCl}$.

Performance of Work

Fill the spectrophotometric planchet with the initial solution of $^{237}\text{Np}^{\text{IV}}$ with the aid of the pipette, add rongalite (10 mg/ml), $\text{N}_2\text{H}_4 \cdot \text{HCl}$ (20 g/litre), and rapidly close the planchet with a tightly fitting cover. Transfer the planchet to the spectrophotometer and visually observe the change in the solution's colour until it becomes violet-light blue. Measure the optical density at wavelengths of 661 and 787.5, 723 and 964 nm at definite intervals of time (minutes). Enter the results of the measurements in a table as shown below:

Ion	λ , nm	D before addition of rongalite	D after addition of rongalite in							
			3-5 min	7-10 min	17-20 min	30 min	1 h	2 h	3 h	4 h
Np^{3+}	661									
	787.5									
Np^{4+}	723									
	964									

Determine the rate of the reaction: slow, fast, or instantaneous.

Again measure the optical density at the same wavelengths and determine the duration of the reaction $\text{Np}^{\text{III}} \rightarrow \text{Np}^{\text{IV}}$ when the reduced solution is standing in the open air. Appraise the content of Np^{IV} (in %) in the solution according to the calibration curve of the optical density against the neptunium concentration.

B. PREPARATION OF Np^{IV}

In oxidation-reduction reactions for preparing Np^{IV} proceeding in definite conditions, one can use reducing agents such as N_2H_4 , NH_2OH , SO_2 , $\text{H}_2\text{C}_2\text{O}_4$, KI and FeSO_4 , and also an equimolar mixture of $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$ and $(\text{NH}_2\text{SO}_2\text{O})_2\text{Fe}$ (sulphamate of Fe^{II}) at room temperature. An example is the method of preparing Np^{IV} by reducing Np^{V} with the aid of hydrazine in solutions of HClO_4 and HNO_3 .

Equipment and Reagents

Equipment and Utensils. A spectrophotometer (SF-4, SF-6). A rectangular quartz or glass planchet with an absorbing layer 1 cm thick. A water bath. An analytical balance. Glass test tubes for 10 ml (2). A capillary pipette for 2-3 ml.

Radioactive Substances. A solution containing 0.007 mol/litre of $^{237}\text{Np}^{\text{V}}$ and 1-3 M relative to HNO_3 .

Reagents. $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$. A concentrated solution of HNO_3 .

Performance of Work

To 4-5 ml of the initial solution of ^{237}Np in a test tube, add $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$, gradually increasing its concentration to 5 g/litre. Heat the solution on the water bath at 60-70 °C during 30 min, transfer it with the aid of the pipette into the planchet, and photograph the absorption spectrum at wavelength sections of 680-735 and 950-990 nm. When the concentration of the reducing agent is increased from 5 to 20 g/litre, a decrease in the absorption peak is observed at 983 nm and an increase in the peaks at wavelengths of 723 and 964 nm. Convince yourself that upon repeated heating during 30 min at a hydrazine concentration of 20 g/litre the nature of the absorption spectrum no longer changes, which points to the completeness of reduction of the Np^{V} . Determine the nature of the reaction rate: slow, fast, or instantaneous.

The solution obtained, containing Np^{IV} , is stable for a long time. Appraise the content of the Np^{IV} in the solution (in %) with the aid of the calibration curve of the optical density against the neptunium concentration.

C. PREPARATION OF Np^{V}

Solutions of Np^{V} are the most stable. They are usually prepared in the following ways:

(1) by heating solutions of Np^{IV} in 1-2 *N* nitric acid (the formation of a certain amount of Np^{VI} is possible); in 0.1 *N*-0.5 *N* solutions of HNO_3 , the reaction of oxidation of Np^{IV} to Np^{V} at 70 °C proceeds about one hour; the process is accelerated in the presence of insignificant amounts of NaNO_2 (~ 0.05 *M*):

(2) by oxidizing Np^{IV} with a stoichiometric amount of Ce^{IV} ;

(3) by oxidizing Np^{IV} with hydrogen peroxide or sodium nitrite with heating (in 1-2 *N* acid);

(4) by reducing Np^{VI} with a stoichiometric amount of Sn^{II} or a 0.1 *M* solution of hydrazine in the cold in 1-5 *M* nitric acid;

(5) by reducing Np^{VI} in 0.5-3.0 *M* nitric acid with hydrogen peroxide with heating during 5-10 min on a boiling water bath (the reaction proceeds to the end).

Equipment and Reagents

Equipment and Utensils. A spectrophotometer (SF-4, SF-4A, SF-8, etc.). Glass or quartz planchets with an absorbing layer 1 cm thick (3). A water bath. Glass test tubes for 10 ml (3). A capillary pipette for 2-3 ml. Glass rods.

Radioactive Substances. A solution (5 ml) containing 0.002 mol/litre of $^{237}\text{Np}^{\text{IV}}$ and 1 *N* relative to HCl . A solution (5 ml) containing 0.002 mol/litre of $^{237}\text{Np}^{\text{IV}}$ and 1 *N* relative to HNO_3 .

Reagents. NaNO_2 . $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$. NH_2OH . Solutions: 30% H_2O_2 ; concentrated HNO_3 , HCl .

Performance of Work

To 4-5 ml of a solution containing ~ 0.005 mol/litre of Np^{VI} (see Sec. D) and 1 *N* relative to HNO_3 in a test tube, add hydrazine or hydroxylamine dropwise in the cold to a concentration of ~ 0.1 *M* or add 0.5 ml of a 30% solution of H_2O_2 with heating during 5-10 min on the boiling water bath. Next transfer the solution to a planchet and measure the maximum of the optical density near wavelengths of 980-990 nm. Appraise the content of Np^{V} (in %) in the solution with the aid of a calibration curve.

To 4-5 ml of a solution of 1 *N* relative to HNO_3 containing 0.002 mol/litre of $^{237}\text{Np}^{\text{IV}}$ in a test tube, add NaNO_2 to a concentration of 0.1 *M*.

Heat the solution on the water bath at a temperature of 80-90 °C during 15 min. Measure the maxima of the optical

density near wavelengths of 723 and 980-983 nm and appraise the content of Np^{V} (in %) in the solution with the aid of calibration curves of the optical density against the neptunium concentration.

D. PREPARATION OF Np^{VI}

Neptunium(VI) is prepared by oxidizing its lower oxidation states with the aid of oxidizing agents such as HNO_3 , Ce^{IV} , KBrO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$, and NaBiO_3 . Particularly, weighed amounts of Np^{IV} are oxidized with potassium bromate at 25°C in several hours. Elevation of the temperature increases the rate of this reaction. Heating of solutions of a neptunium salt with concentrated nitric acid during three hours leads to the quantitative oxidation of the neptunium to Np^{VI} . In 4 and 7 *M* nitric acid at 95°C , Np^{IV} is oxidized to Np^{VI} in one hour.

Equipment and Reagents

Equipment and Utensils. A spectrophotometer (SF-4, SF-4A, SF-8, SF-16, etc.). Rectangular or quartz planchets with an absorbing layer 1 cm thick (3). A water bath. Glass test tubes for 10 ml (3). A capillary pipette for 2-3 ml. A quartz beaker for 10-15 ml. A watch glass.

Radioactive Substances. A solution, 0.5 *N* relative to HNO_3 and containing ~ 0.005 mol/litre of $^{237}\text{Np}^{\text{IV}}$. A solution, 0.5 *N* relative to H_2SO_4 and containing ~ 0.006 mol/litre of $^{237}\text{Np}^{\text{IV}}$.

Reagents. KBrO_3 . Solutions: 13-14 *M* HNO_3 ; concentrated H_2SO_4 .

Performance of Work

(a) Oxidation with Nitric Acid

To 4-5 ml of a solution containing ~ 0.005 mol/litre of $^{237}\text{Np}^{\text{IV}}$ and 1 *N* relative to HNO_3 in a quartz beaker add about the same volume of concentrated (13-14 *M*) nitric acid. Heat the solution with boiling, after covering the beaker with the watch glass, during 3-4 h. Next remove the surplus acid by evaporation, dilute the solution to a concentration (with respect to Np^{VI}) convenient for spectrophotometric measurement, and transfer it into a planchet with the aid of the capillary pipette. Measure the optical density at 476 and 557 nm and determine the amount of neptunium

(in %) oxidized to the hexavalent state. For a quantitative appraisal of the Np^{VI} content, preliminarily plot a calibration curve of the optical density at the selected wavelength against the concentration of the Np^{VI} in the solution.

(b) Oxidation with Potassium Bromate

To 4-5 ml of a solution of 1 *N* relative to H_2SO_4 containing 0.005 mol/litre of Np^{IV} in a test tube, add KBrO_3 to a concentration of about 0.1 *M*, keep the solution at room temperature for 2.5 h, and then on the water bath at 35 °C for one hour.

Use the previously obtained calibration curve to determine the oxidation state of the neptunium by measuring the optical density of the solution at the given wavelength.

E. PREPARATION OF Np^{VII}

To prepare Np^{VII} , oxidizers such as ozone, $\text{K}_2\text{S}_2\text{O}_8$, NaBrO , ferricyanide ions, silver oxides, permanganate, periodate, bismuthate, and other ions are used in alkaline solutions. The rate and the completeness of the oxidation reaction $\text{Np}^{\text{VI}} \rightarrow \text{Np}^{\text{VII}}$ depend on the concentration of the alkali, the oxidizing agent, and the temperature, most reagents being sufficiently effective at a moderate concentration of the alkali (1-3 *M*). Examples of other known methods are the disproportionation of Np^{VI} and the electrolysis of alkaline solutions of Np^{VI} or suspensions of neptunates.

Equipment and Reagents

Equipment and Utensils. A spectrophotometer (SF-4, SF-4A, SF-8, etc.). An ozonizer. Glass or quartz planchets with an absorbing layer 1 cm thick (3). A water bath. Glass test tubes for 10-15 ml (5). A capillary pipette for 2-3 ml.

Radioactive Substances. A suspension of sodium neptunate or of NpO_2OH in a solution of 1 *N* NaOH . A solution (~ 10 ml) containing $\sim 2 \times 10^{-4}$ mol/litre of $^{237}\text{Np}^{\text{VI}}$ (the mother liquor after separating the neptunate or hydroxide precipitate).

Reagents. Ozone. FeCl_3 . $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. $\text{K}_2\text{S}_2\text{O}_8$. NaBrO . $\text{K}_3\text{Fe}(\text{CN})_6$. KMnO_4 . NaBiO_3 . KIO_4 . Solutions: 1 *N* and 2-3 *N* NaOH ; concentrated NaOH , KOH .

Performance of Work

(a) Add 4-5 ml of a 2-3 *N* solution of NaOH to a suspension of sodium neptunate or NpO_2OH in a test tube and perform ozonization of the solution at room temperature up to the appearance of an intensive yellowish-green colour in it.

(b) Add $\text{K}_2\text{S}_2\text{O}_8$ up to a concentration of 0.1 *M* to 4-5 ml of a solution containing about 2×10^{-4} mol/litre of $^{237}\text{Np}^{\text{VI}}$ (the mother liquor after separation of the neptunate or hydroxide precipitate) and 0.1-0.7 *N* with respect to NaOH in a test tube and heat the solution to above 50 °C.

(c) Prepare 4-5 ml of the initial solution containing about 2×10^{-4} mol/litre of $^{237}\text{Np}^{\text{VI}}$ [as indicated in clause (b)] in a test tube. Prepare Np^{VII} by one of the following methods:

1. Add NaOH up to a concentration of 3-4 *N* and NaBrO up to a concentration of 0.05-0.1 *M* to the initial solution with heating at 60-80 °C.

2. Add KOH up to a concentration exceeding 6 *M* and $\text{K}_3\text{Fe}(\text{CN})_6$ up to a concentration of about 1×10^{-3} *M* to the initial solution at room temperature.

3. Add NaOH up to a concentration of 3-4 *M* and KMnO_4 (~ 0.05 *M*) to the initial solution at room temperature.

4. Add KOH up to a concentration of 5 *M* and potassium periodate or sodium bismuthate up to a concentration of 0.1 *M* to the initial solution attended by heating up to 85 °C.

Determine the oxidized fraction of the Np^{VI} by measuring the optical density of the solution at 440 and 620 nm. Use the results of measuring D_{max} and visual observation of the change in the colour of the solutions to arrive at conclusions on the nature of the reaction rate: slow, fast or instantaneous.

For a slow reaction, determine the duration of oxidation of half of the Np^{VI} .

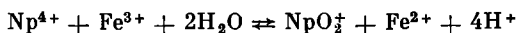
When performing operation (b), also determine the influence of:

- (1) the concentration of the alkali;

- (2) additions of ions (in 4 *M* NaOH) of transition metals— Fe^{III} at a concentration of 5×10^{-5} *M* and Co^{II} at a concentration of 2×10^{-8} *M* as reaction catalysts.

Experiment 14.2. KINETICS OF OXIDATION-REDUCTION REACTIONS OF NEPTUNIUM [1]

To know the oxidation-reduction properties of neptunium ions, as of other actinides, one must derive the kinetic equations and determine the rate constants of the reactions of their transitions from one oxidation state to another. We can give as an example of investigations of this kind the problem of determining the rate constant of the reaction of oxidizing Np^{IV} with iron(III):



This reaction is reversible and proceeds in both directions at a measurable rate at room temperature. To shift equilibrium to the right, one must add to the solution ammonium persulphate or sodium nitrite ($\sim 0.05\text{ M}$), which rapidly oxidize the Fe^{II} , but react extremely slowly with the Np^{IV} . The rate of the forward reaction in an HNO_3 solution observes the equation

$$-\frac{d[\text{Np}^{\text{IV}}]}{dt} = k \frac{[\text{Np}^{\text{IV}}][\text{Fe}^{\text{III}}]}{[\text{H}^+]^3}$$

where $k = 0.49\text{ M}^2 \cdot \text{min}^{-1}$ at 25°C and an ionic strength of the solution of $\mu = 2$ [1].

Equipment and Reagents

Equipment and Utensils. A spectrophotometer (SF-4, SF-4A, SF-8, etc.) provided with a thermostated planchet holder. Glass or quartz planchets with an absorbing layer 1 cm thick (2). Glass test tubes for 10 ml (2). A capillary pipette for 2-3 ml.

Radioactive Substances. A solution, 1-2 N with respect to HNO_3 , containing ~ 0.01 mol/litre of $^{237}\text{Np}^{\text{IV}}$.

Reagents. NaNO_3 , NaNO_2 or $(\text{NH}_4)_2\text{S}_2\text{O}_8$. An approximately 0.5 M nitric acid solution of $\text{Fe}(\text{NO}_3)_3$ prepared by dissolving pure (better electrolytic) iron in HNO_3 ; concentrated HNO_3 .

Performance of Work

Pour a solution containing $\sim 4 \times 10^{-3}$ mol/litre of $^{237}\text{Np}^{\text{IV}}$ and 1 N with respect to HNO_3 into a working planchet, next add NaNO_3 (for maintaining a constant ionic strength) and NaNO_2 [or $(\text{NH}_4)_2\text{S}_2\text{O}_8$] up to a concentration of 1 M and $\sim 0.05\text{ M}$ respectively. Stir the solution and measure its optical density at 723 and 980 nm, seeing that the Np^{IV}

is not oxidized. After this, add a solution of $\text{Fe}(\text{NO}_3)_3$ with a concentration of 0.05 M and register the optical density at 723 nm as a function of the time.

To determine the first-order rate constant, plot $\log D$ against the time and use the slope of the resulting straight line to calculate the constant (in min^{-1}): $k' = 2.3 \tan \alpha$. Run an experiment in a similar way at another concentration of the $\text{Fe}(\text{NO}_3)_3$ and according to the results of both experiments calculate the second-order rate constant (in $M^{-1}\text{min}^{-1}$) by the formula $k_1 = k'/[\text{Fe}^{\text{III}}]$.

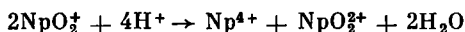
The overall rate constant of the reaction (in $M^2\text{min}^{-1}$) is determined from the equation

$$k = k' \frac{[\text{H}^+]^3}{[\text{Fe}^{\text{III}}]}$$

Compare it with the value in the literature [1].

Experiment 14.3. DISPROPORTIONATION OF Np^{V} [1, 3, 4]

Neptunium(V) disproportionates to an insignificant extent in 1 N solutions of HCl and HClO_4 :



The rate of the process grows greatly when the acidity of the solution increases. In solutions of H_2SO_4 , where Np^{IV} forms quite stable complex compounds with the SO_4^{2-} ion, equilibrium of the reaction shifts in the direction of formation of Np^{IV} and Np^{VI} .

Disproportionation of Np^{V} in solutions of HClO_4 at a concentration of it from about 5.3 to 8.7 M proceeds quite rapidly (the values of the concentration constants $K = [\text{Np}^{\text{IV}}][\text{Np}^{\text{VI}}]/[\text{Np}^{\text{V}}]^2$ are within the interval from 0.13 to 200).

Equipment and Reagents

Equipment and Utensils. A spectrophotometer (SF-4, SF-4A, SF-8, etc.). A rectangular quartz or glass planchet with an absorbing layer 1 cm thick. A thermostat. Glass test tubes for 10 ml (2). A capillary pipette for 2-3 ml.

Radioactive Substances. 10 ml of a 1 N solution with respect to HClO_4 containing $\sim 10^{-4}$ mol/litre of $^{237}\text{Np}^{\text{V}}$.

Reagents. A concentrated solution of HClO_4 .

Performance of Work

Prepare solutions of the following compositions in test tubes (4-5 ml of each):

(1) 7.0 *M* relative to HClO_4 containing 0.005 mol/litre of $^{237}\text{Np}^{\text{V}}$;

(2) 8.5 *M* relative to HClO_4 containing 0.007 mol/litre of $^{237}\text{Np}^{\text{V}}$.

Keep the solutions at a constant temperature ($25 \pm 0.1^\circ\text{C}$), regularly determining the concentrations of various oxidation states of the neptunium (in 1, 2, 4, 18, 24 h, and so on), until equilibrium sets in between all the oxidation states.

To determine the concentration of each oxidation state, carefully transfer the solution with the aid of a pipette into a quartz planchet and measure the optical density D at wavelengths of 723 and 983 nm, corresponding to the main absorption peaks of Np^{IV} and Np^{V} . According to the experimental results of measuring D_{723} and D_{983} depending on the time elapsed from the beginning of the experiment, calculate the concentrations of Np^{IV} and Np^{V} (c_{IV} and c_{V}) by solving the simultaneous equations

$$\left. \begin{aligned} D_{723} &= \varepsilon'_{\text{IV}} c_{\text{IV}} + \varepsilon'_{\text{V}} c_{\text{V}} \\ D_{983} &= \varepsilon''_{\text{IV}} c_{\text{IV}} + \varepsilon''_{\text{V}} c_{\text{V}} \end{aligned} \right\} \quad (14.1)$$

where ε'_{IV} and ε'_{V} are the molar absorption coefficients of solutions containing Np^{IV} and Np^{V} at $\lambda = 723$ nm, and $\varepsilon''_{\text{IV}}$ and ε''_{V} are the same at $\lambda = 983$ nm.

The values of the molar absorption coefficients of solutions containing Np^{IV} and Np^{V} at given wavelengths are determined preliminarily or are taken from reference publications.

Calculate the content of Np^{VI} in a solution according to the difference between the initial concentration of the neptunium and the total concentration of the Np^{IV} and Np^{V} . To determine the content of Np^{IV} and Np^{V} (in %), also use the calibration curves $D_{723} = f(c_{\text{IV}})$ and $D_{983} = f'(c_{\text{V}})$.

Next evaluate the concentration equilibrium constant and determine the duration of disproportionation by 50% — $-t_{1/2}$ (see Experiment 15.4). By comparing the obtained values of K and $t_{1/2}$ for two concentrations of the HClO_4 in the solutions, determine the influence of the hydrogen ion

concentration on the rate and completeness of the reaction of disproportionation of Np^{V} .

Enter the experimental and calculated data into a table as follows:

Time from beginning of experiment, h	$[\text{Np}^{\text{IV}}]$, mol/litre	$[\text{Np}^{\text{V}}]$, mol/litre	$[\text{Np}^{\text{VI}}]$, mol/litre	$[\text{Np}^{\text{IV}}]$, %	$[\text{Np}^{\text{V}}]$, %	$[\text{Np}^{\text{VI}}]$, %	$\sum [\text{Np}]$, calc, %	$K = \frac{[\text{Np}^{\text{IV}}][\text{Np}^{\text{VI}}]}{[\text{Np}^{\text{V}}]^2}$

Use the data obtained to plot graphs of the neptunium content (in %) in a certain oxidation state against the time elapsed from the instant of beginning to measure the optical density.

Experiment 14.4. DISTRIBUTION OF Np IN AN AQUEOUS SOLUTION-SOLID PHASE SYSTEM [5-7]

Coprecipitation plays a major role in studying the chemistry and analytical chemistry of neptunium. Table 14.2

Table 14.2. Coprecipitation of Indicator Amounts of Neptunium (q = quantitative coprecipitation, n = no coprecipitation, p = partial coprecipitation)

Carrier	Coprecipitation		
	Np^{IV}	Np^{V}	Np^{VI}
Hydroxides	q	q	q
Lanthanum fluoride	q	n	n
Lanthanum oxalate	n	q	—
Potassium and lanthanum double sulphate	q	—	n
Sodium uranyltriacetate	n	p	q
Thorium benzenesulphinate	q	—	
Thorium iodate	q	—	n
Thorium oxalate	q	n	n
Thorium peroxide	q	—	—
Zirconium phenylarsonate	q	—	n
Zirconium phosphate	q	—	—

presents data characterizing the ability of neptunium ions to coprecipitate with certain carriers.

A. COPRECIPITATION OF Np^{IV} WITH POTASSIUM AND LANTHANUM DOUBLE SULPHATE

Neptunium(IV) coprecipitates well with $\text{K}_3\text{La}(\text{SO}_4)_3$, dissolving with difficulty in saturated solutions of K_2SO_4 , whereas Np^{VI} does not coprecipitate in these conditions. This property of neptunium underlies the sulphate method of separating a mixture of radioelements and recovering Np^{IV} from dilute solutions.

Equipment and Reagents

Equipment and Utensils. A counting installation with a detector of α -radiation and an end-window counter. A centrifuge. A device for preparing SO_2 . A liquid proportioner (or a micropipette with syringe adjustment). Measuring cylinders for 100 ml (2). Glass rods. A calibrated pipette for 10 ml with a syringe or capillary pipette for 2-3 ml.

Radioactive Substances. 1-2 ml of a 0.1 *N* solution relative to HNO_3 containing ^{239}Np with a specific activity of $\sim 10^6$ cpm/ml, or 3-4 ml of a 1 *N* solution relative to HNO_3 containing $\sim 1 \times 10^{-4}$ mol/litre of ^{237}Np .

Reagents. 5-7% solution of HNO_3 . SO_2 . $\text{La}(\text{NO}_3)_3$. K_2SO_4 .

Performance of Work

In a 100-ml measuring cylinder, prepare 30-40 ml of an initial solution containing an indicator amount of ^{239}Np ($\sim 10^4$ cpm/ml) or ^{237}Np ($\sim 10^3$ cpm/ml) and 0.2-0.3 mg of La per ml of solution, 5-7% relative to HNO_3 , and $\sim 1\%$ relative to SO_2 .

Reduce the neptunium during one hour at room temperature, after which saturate the solution with potassium sulphate. Let the precipitate settle (>10 h) and separate the phases by decanting or removing the solution with the aid of a pipette.

Evaluate the fraction of the coprecipitated Np^{IV} according to the neptunium concentration in the solution before and after the precipitation of $\text{K}_3\text{La}(\text{SO}_4)_3$ determined by the radiometric method. Determine the crystallization coefficient by prolonged recrystallization of the $\text{K}_3\text{La}(\text{SO}_4)_3$ precipitate (up to the establishment of true equilibrium between the crystals and solution at 20°C).

B. COPRECIPITATION OF Np^{VI} WITH SODIUM URANYLTRIACETATE

Neptunium(VI) coprecipitates well with $\text{NaUO}_2(\text{CH}_3\text{COO})_3$, whereas Np^{IV} does not coprecipitate, while Np^{V} may coprecipitate only partly.

Equipment and Reagents

Equipment and Utensils. A counting installation with a detector of α -radiation and an end-window counter. A water bath. A liquid proportioner. Measuring cylinders for 100 ml (3). Conical flasks for 100-200 ml (4). Glass rods. Calibrated or capillary pipettes (3). Chemical beakers.

Radioactive Substances. A 0.05 *N* solution relative to HNO_3 (1-2 ml) containing ^{239}Np with a specific activity of $\sim 10^6$ cpm/ml, or three or four 1 *N* solutions relative to HNO_3 containing $\sim 1 \times 10^4$ mol/litre of ^{237}Np .

Reagents. $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$. $(\text{NH}_2\text{SO}_2\text{O})_2\text{Fe}$. NaNO_2 . Solutions: KMnO_4 . 1 *N* and 3-5 *M* HNO_3 ; saturated CH_3COONa .

Performance of Work

To 30-40 ml of the initial solution, 0.05 *N* relative to HNO_3 containing indicator amounts of ^{239}Np ($\sim 10^4$ cpm/ml) or ^{237}Np ($\sim 10^3$ cpm/ml) and macroamounts of uranium (5-10 g/litre) add several drops of a dilute (1 mg/ml) solution of KMnO_4 (up to the appearance of a non-vanishing colour) to stabilize the Np^{VI} . After heating on the water bath for 10-15 min, pour in an equal volume of a saturated solution of CH_3COONa to the initial solution. Stir the precipitate of sodium uranyltriacetate with a glass rod, let it stand for 30 min, after which decant the solution or carefully remove it with a pipette. Wash the precipitate twice with a saturated solution of CH_3COONa , combine the mother and washing solutions for determining their neptunium content. Next dissolve the precipitate in a minimum volume of 3-5 *M* nitric acid in the cold or if necessary with heating, and determine the content of Np^{VI} in the solution by the radiometric method, and then calculate the degree of its coprecipitation (in %).

Perform similar precipitations of $\text{NaUO}_2(\text{CH}_3\text{COO})_3$ from solutions containing Np^{IV} and Np^{V} , and use the results of the experiment to determine the nature and degree of coprecipitation of neptunium in different

oxidation states. To stabilize the Np^{IV} , add 0.2-0.3 mol/litre of $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$ to the initial solution, heat the solution on the water bath at 80-90 °C for about 30 min, and after cooling add 0.01 mol/litre of $\text{Fe}(\text{II})$ sulphamate.

To obtain and stabilize Np^{V} , heat the initial solution in the presence of NaNO_2 (~ 0.1 mol/litre) on the water bath at 50-60 °C during 15-20 min.

C. COPRECIPITATION OF Np^{V} WITH IRON HYDROXIDE

The degree of coprecipitation of a metal ion with iron hydroxide is affected by factors such as the mass of the collector, the concentration of the microcomponent and neutral electrolyte, and the pH of the solution. In this case, the distribution coefficient has the form

$$K_d = \frac{(a_0 - a_{\text{eq}}) V}{a_{\text{eq}} m_c}$$

where a_0 and a_{eq} are the specific activities of the initial and equilibrium solutions, respectively, V is the volume of the liquid phase, ml, and m_c is the mass of the collector, g.

In addition to K_d , the coprecipitation (in %) is also sometimes given:

$$S = \frac{K_d}{K_d + (V/m_c)} 100\%$$

and also the value of the sorption ratio (or partition function):

$$\bar{e} = \frac{S}{100\% - S}$$

Equipment and Reagents

Equipment and Utensils. A counting installation with a detector of α -radiation and an end-window counter. An electronic potentiometer (LPU-04) or a laboratory pH meter ("pH 673"). A liquid proportioner. Measuring cylinders for 250 ml (5). Glass rods. Calibrated or capillary pipettes (2).

Radioactive Substances. A 0.1 N solution relative to HNO_3 (4-5 ml) containing ^{239}Np with a specific activity of $\sim 10^6$ cpm/ml or a 0.1 N solution relative to HNO_3 containing $\sim 1 \times 10^{-3}$ mol/litre of ^{237}Np .

Reagents. NaNO_2 . NH_4Cl . $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Solutions: concentrated HNO_3 , NH_4OH .

Performance of Work

In each of the five measuring cylinders, prepare 100 ml of a nitric acid solution ($\text{pH} \sim 2-3$) containing tracer amounts of $^{239}\text{Np}^{\text{V}}$ ($\sim 10^4$ cpm/ml) or ^{237}Np ($\sim 10^3$ cpm/ml), sodium nitrite (0.05 M), and ammonium chloride (0.5 M). Add varying amounts of a collector— $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ within the concentration interval of 1.8×10^{-6} to 2.5×10^{-3} mol/litre to these solutions. Next with stirring during the first 1-2 min, precipitate iron hydroxide by adding NH_4OH to a pH of about 8.5. Establish the pH of the solutions with the aid of the pH meter. After settling of the precipitate for about 30 min, separate it from the solution by decantation or centrifuging for about 5 min at 6000 rpm. Determine the distribution of the Np^{V} between the precipitate and the solution according to the ratio of the β -activity (or α -activity when using ^{237}Np) of the clarified solution obtained by decanting or centrifuging and of the initial solution. Calculate the values of K_d and $\bar{\epsilon}$, find the graphical relation between $\log \bar{\epsilon}$ and $\log [m_c]$ and the slope of the straight line obtained. Determine the nature of the linear isotherm (of the Henry or Langmuir type).

Experiment 14.5. DISTRIBUTION OF Np BETWEEN WATER AND AN ORGANIC SOLVENT [8-10]

The extraction of neptunium in various oxidation states is widely used both when developing extraction methods of recovering this element from irradiated uranium and when studying its physicochemical properties.

A. EXTRACTION WITH TRIBUTYLPHOSPHATE

Tributylphosphate (TBP) is the most convenient extracting agent of neptunium. To remove dibutylphosphate impurities, TBP before use is treated with a dilute solution of Na_2CO_3 or alkali with the following washing with dilute nitric acid. Extraction is usually performed with 10-30% TBP in another solvent, for example in CCl_4 or benzene. Tributylphosphate extracts both Np^{IV} and Np^{VI} well; Np^{V} is not extracted to a noticeable extent.

Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window counter. A water bath. A liquid proportioner. A separatory funnel. Test tubes for 10 ml (5). Conical flasks for 250 ml (4). A pipette with a syringe.

Radioactive Substances. 5-10 ml of a 2 *N* solution relative to HNO_3 containing ^{239}Np with a specific activity of $\sim 10^5$ cpm/ml. (If there is no preparation of ^{239}Np in the laboratory, a preparation of ^{237}Np may be used.)

Reagents. $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$, $(\text{NH}_2\text{SO}_2\text{O})_2\text{Fe}$, NaNO_2 , Na_2CO_3 , NaOH . Solutions: purified 20% TBP in kerosene or synthine; 2 *N* and 7 *M* HNO_3 ; dilute (1 mg/ml) KMnO_4 ; concentrated H_3PO_4 .

Performance of Work

Pour 5-10 ml of the initial 2 *N* solution relative to HNO_3 containing indicator amounts of ^{239}Np (10^4 cpm/ml) into each of three test tubes. To obtain Np^{IV} , add 0.2 mol/litre of $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$ to the initial solution, heat the solution in a test tube on the water bath at 80-90 °C during 30 min and then after cooling add ~ 0.01 mol/litre of iron(II) sulphamate. To stabilize Np^{V} , heat the solution in another test tube in the presence of NaNO_2 (~ 0.1 *M*) at 50-60 °C during 15-20 min; prepare Np^{VI} by adding to the solution a few drops of a dilute (1 mg/ml) solution of KMnO_4 until a non-vanishing colour appears and then heating the solution during 10-15 min.

Next consecutively transfer the solutions by means of the pipette with the syringe into the separatory funnel and perform extraction with an equal volume of a 20% solution of TBP in kerosene or synthine (preliminarily wash with a solution of Na_2CO_3 or NaOH , and then HNO_3) while vigorously shaking during 5 min at room temperature. After settling and separation of the phases, take samples (0.09 ml from each phase) and measure the β -activity in them. Evaluate the degree of extraction of Np^{IV} , Np^{V} , and Np^{VI} into the organic phase (in %).

Determine how the extraction of Np^{IV} is affected by the concentration of the TBP, the salting out agent, the HNO_3 , and the complexing agent. For this purpose, prepare the following solutions containing indicator amounts of $^{239}\text{Np}^{\text{IV}}$ (10^4 cpm/ml):

- (1) 7 *M* relative to HNO_3 , ~ 0.2 *M* relative to $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$, 0.01 *M* relative to $(\text{NH}_2\text{SO}_2\text{O})_2\text{Fe}$;
- (2) 2 *N* relative to HNO_3 , 4 *M* relative to NH_4NO_3 ,

$\sim 0.2 M$ relative to $N_2H_4 \cdot HNO_3$, $\sim 0.01 M$ relative to $(NH_2SO_2O)_2Fe$;

(3) $2 N$ relative to HNO_3 ; $\sim 0.2 M$ relative to $N_2H_4 \cdot HNO_3$; $\sim 0.01 M$ relative to $(NH_2SO_2O)_2Fe$, $0.5 M$ relative to H_3PO_4 .

After heating these solutions in test tubes on the water bath at $80-90^\circ C$ for 30 min and cooling them to room temperature, perform consecutive extraction with equal initial volumes of a 20% solution of TBP in kerosene or synthine. Also perform extraction with a 10% solution of TBP from the first or second solution. When comparing the obtained distribution coefficients of Np^{IV} , determine the influence of various factors on the extraction process.

Reextract neptunium by washing the organic phase with solutions that transfer the neptunium to the pentavalent state.

B. EXTRACTION WITH AMINES

Neptunium can be successfully extracted from nitric acid solutions with dilute solutions of tri-*N*-octylamine (TOA), trilaurylamine, and tri-*iso*-octylamine.

Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window counter. A water bath. A liquid proportioner. Separatory funnels. Test tubes for 10 ml (6). Conical flasks for 250 ml (4). A pipette with a syringe.

Radioactive Substances. A solution (5-10 ml) of 1-2 *N* relative to HNO_3 containing ^{239}Np with a specific activity of $\sim 10^5$ cpm/ml.

Reagents. $N_2H_4 \cdot HNO_3$. $(NH_2SO_2O)_2Fe$. $NaNO_2$. $KBrO_3$. Tri-*N*-octylamine. Tri-*iso*-octylamine. Xylene. Solutions: 0.5, 1, and 2 *N*, 4 and 10 *M* HNO_3 , 4 *M* NH_4NO_3 .

Performance of Work

Prepare the following initial solutions containing tracer amounts ($\sim 10^4$ cpm/ml) of $^{239}Np^V$ in test tubes (5-10 ml in each):

- (1) 2 *N* relative to HNO_3 , 0.2 *M* relative to $N_2H_4 \cdot HNO_3$;
- (2) 4 *M* relative to HNO_3 , 0.2 *M* relative to $N_2H_4 \cdot HNO_3$;
- (3) 2 *N* relative to HNO_3 , 0.1 *M* relative to $NaNO_2$;
- (4) 10 *M* relative to HNO_3 , 0.1 *M* relative to $NaNO_2$;
- (5) 2 *N* relative to HNO_3 , 0.2 *M* relative to $KBrO_3$;
- (6) 4 *M* relative to HNO_3 , 0.2 *M* relative to $KBrO_3$.

To stabilize the Np^{IV} , heat the initial solutions 1 and 2 in the test tubes on the water bath at 80-90 °C during 30 min, and then after cooling add ~ 0.01 mol/litre of iron(II) sulphamate to them.

Heat the initial solutions 3 and 4 on the water bath at 50-60 °C during 15-20 min, thus stabilizing the Np^{V} .

To prepare Np^{VI} , heat solutions 5 and 6 at 80-90 °C during 15 min.

Transfer the solutions with the aid of the pipette with the syringe into separatory funnels and extract the neptunium with an equal volume of a 20% solution of TOA (preliminarily wash two or three times with an equal volume of a solution having the same composition as the initial one, but without the Np) in xylene with vigorous shaking during 3-5 min at room temperature. Next (after settling for five minutes) separate the phases and take samples (0.09 ml each) with the aid of the liquid proportioner for measuring the β -activity of the neptunium. Calculate the degree of extraction (in %) and the separation coefficients of Np^{IV} , Np^{V} , and Np^{VI} .

To reextract the neptunium, treat the organic phase by shaking with water and 1 *N* nitric acid in the presence of NaNO_2 (0.1 *M*).

Using a similar procedure, extract Np^{IV} , for example, with a 0.2 *M* solution of tri-*iso*-octylamine in xylene from solutions of:

(1) 0.5 *N* relative to HNO_3 .

(2) 0.5 *N* relative to HNO_3 , 4 *M* relative to NH_4NO_3 .

On the basis of the found values of the distribution coefficients, establish the influence of the concentration of HNO_3 and the salting out agent on the extraction of neptunium.

C. EXTRACTION WITH HYDROXYLAMINE DERIVATIVES

Neptunium(V) is extracted quite well by neocupferron and benzoylphenylhydroxylamine (BPHA). The degree of extraction of Np^{V} depends greatly on the nature of the extractant solvent used and on the pH of the initial solution. The extraction of neptunium is hindered by the presence of complexing agents (carbonates, phosphates, acetates, etc.).

Prior to extraction, the neocupferron is purified from the decomposition products by dissolving the reagent in a small

amount of alcohol with the following precipitation with ether.

The organic solvents used in the experiment are purified by distillation.

Equipment and Reagents

Equipment and Utensils. A counting installation with a scintillation or semiconductor detector of α -radiation and an end-window counter. A lamp potentiometer (LP-58, LPU-01) or a laboratory pH meter ("pH 673"). A water bath. A shaking apparatus or a vibrator controlled with the aid of an autotransformer. A chromatographic column. A liquid proportioner. Separatory funnels (4). Graduated test tubes for 20-25 ml with ground-glass stoppers (5). Conical flasks for 100-200 ml (4). A pipette with a syringe. Beakers for 20-30 ml (5).

Radioactive Substances. ~ 10 ml of an initial solution, 0.05 N relative to HNO_3 , containing $^{239}\text{Np}^{\text{V}}$ with a specific activity of $\sim 10^5$ cpm/ml or ^{237}Np ($\sim 10^3$ cpm/ml).

Reagents. Diethyl ether. Hexyl and butyl alcohols. Butylamine. Chloroform. NaNO_2 . $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$. Solutions: 0.1 M BPHA, 0.01 M neocupferron; dilute NH_4OH ; 0.05 N HNO_3 .

Performance of Work

(a) Extraction of Np^{V} with Solutions of BPHA and Neocupferron

Heat the initial solution (10-15 ml), 0.05 N relative to HNO_3 , containing $^{239}\text{Np}^{\text{V}}$ ($\sim 10^4$ cpm/ml) or ^{237}Np ($\sim 10^3$ cpm/ml) with NaNO_2 ($\sim 0.05 M$) on the water bath at 50-60 $^{\circ}\text{C}$ during 15 min. Next bring the pH of the solution up to about 9.0 with the aid of the pH meter and extract the Np^{V} with a solution containing 0.1-0.01 mol/litre of benzoylphenylhydroxylamine in hexanol, shaking the test tube during 30 min at room temperature. After settling, measure the β -activity of the aqueous and organic phases and the pH of the equilibrium solution (potentiometer). In a similar way, extract the Np^{V} with a solution of neocupferron ($\sim 0.01 M$) at a pH of 5.5.

The Np^{V} can be extracted from these solutions in the presence of 0.05% butylamine, which increases the degree of extraction.

Determine the coefficients of distribution and the degree of extraction of the Np^{V} (in %).

*(b) Dependence of Extraction of Np^{V} and Np^{IV}
with BPHA Solution on Concentration of HNO_3*

Prepare 10-15 ml each of solutions containing $^{239}\text{Np}^{\text{IV}}$ and $^{239}\text{Np}^{\text{V}}$ ($\sim 10^4$ cpm/ml) of the following composition:

- (1) Np^{IV} , 0.5 *N* relative to HNO_3 ;
- (2) Np^{IV} , 1 *N* relative to HNO_3 ;
- (3) Np^{IV} , 2 *N* relative to HNO_3 ;
- (4) Np^{V} , 1 *N* relative to HNO_3 ,
- (5) Np^{V} , 2 *N* relative to HNO_3 ;
- (6) Np^{V} , 5 *M* relative to HNO_3 .

Introduce aliquot portions of these solutions into 20-25 ml graduated separatory funnels and extract with an equal volume of BPHA (0.1-0.01 *M*), shaking during 0.5 min at room temperature. After extraction, take aliquot portions for measuring the β -activity of the neptunium in the aqueous and organic phases. Evaluate the distribution coefficients for Np^{IV} and Np^{V} and determine how the concentration of the HNO_3 affects their extraction with the aid of BPHA.

**Experiment 14.6. DISTRIBUTION OF
 Np BETWEEN SOLUTION AND ION EXCHANGER [11]**

Ion exchange has found widespread application in studying the chemical behaviour of actinides, including neptunium. Ion exchange is widely used in laboratories as a method of analysing U, Np, Pu, and their fission products.

A. DISTRIBUTION OF Np^{IV}

Neptunium(IV) is absorbed by cation exchangers in the form of simple or positively charged complex ions. The degree of sorption of Np^{IV} on the cation exchanger is determined by the conditions of running the experiment.

Equipment and Reagents

Equipment and Utensils. A counting installation with a scintillation or semiconductor detector of α -radiation and an end-window counter. A water bath. A shaker. A liquid proportioner. Test tubes or measuring flasks for 50 ml with ground-glass stoppers (10), a test tube for 10 ml.

Radioactive Substances. A solution containing ^{239}Np separated from 50 mg of $\text{UO}_2(\text{NO}_3)_2$ irradiated by an integral flux of neutrons

of $\sim 10^{17}$ cps/cm², or 1-2 ml of a 0.5 *N* solution relative to HNO₃ containing $\sim 1 \times 10^{-4}$ mol/litre of ²³⁷Np.

Reagents. The cation exchanger KU-2 in the NH₄⁺ form (grain size 50-70 mesh). (NH₄ClO₄·N₂H₄·HNO₃). (NH₄SO₄O)₂Fe. Solutions: 1 and 2 *N* HNO₃, 0.1 *N* HClO₄; ~ 10 *M* H₃PO₄.

Performance of Work

Take 1-2 ml of a 0.5 *N* solution relative to HNO₃ containing ²³⁹Np (with a specific activity of $\sim 10^6$ cpm/ml) or ²³⁷Np ($\sim 10^3$ cpm/ml). To obtain the neptunium in the tetravalent state, heat the solution in the presence of N₂H₄·HNO₃ (0.2-0.3 *M*) on the water bath at 80-90 °C for 30 min, and after cooling, add to it ~ 0.01 mol/litre of Fe(II) sulphamate. Next into each of two dry test tubes with ground-glass stoppers introduce 250 mg of the cation exchanger and 10-15 ml of a solution having the composition:

(1) 0.1 *N* relative to HClO₄, 0.4 *M* relative to NH₄ClO₄ (ionic strength 0.5);

(2) 0.1 *N* relative to HClO₄, 0.9 *M* relative to NH₄ClO₄ (ionic strength 1.0).

Add to each tube 0.1 ml of the solution containing ²³⁹Np^{IV}. Mix the contents of the test tubes in the shaker during four hours (until equilibrium is reached in the solutions being studied). In similar conditions, mix standard solutions of the same composition and concentration, but containing no resin. After shaking, take samples (0.09 ml each) for radio-metric determination of the Np^{IV} content in the solutions being studied and in the standard ones.

Calculate the distribution coefficients by the equation

$$K_d = \frac{100 - [\text{Np}]_{\text{us}}}{[\text{Np}]_{\text{us}}} \cdot \frac{V}{m}$$

where $[\text{Np}]_{\text{us}}$ is the amount of unsorbed neptunium in the solution, %, *V* is the volume of the solution, ml, and *m* is the mass of the resin, mg.

Use the obtained data to determine the influence of the salt composition of the solution (the ionic strength) on the distribution coefficient.

In a similar way, determine the relative sorption ability of Np^V and Np^{VI} at an ionic strength of the solutions of 0.1 and 0.5. To stabilize the Np^V, add NaNO₂ to the solutions, and to stabilize the Np^{VI}—KBrO₃ in a concentration of about 0.05 *M*.

B. SORPTION AND ELUTION OF Np^{V}

Np^{V} is sorbed on cation exchangers from dilute solutions of HCl or HNO_3 ($<0.1\text{ M}$). The Np^{V} is desorbed from the resin with moderately concentrated solutions of acids.

Equipment and Reagents

Equipment and Utensils. A counting installation with a scintillation or semiconductor detector of α -radiation and an end-window counter. A water bath. A chromatographic column 35 cm long and 0.5 cm in diameter. A set of test tubes or chemical beakers for 10 ml.

Radioactive Substances. A preparation of ^{239}Np separated from 50 mg of $\text{UO}_2(\text{NO}_3)_2$ irradiated by an integral flux of neutrons of about 10^{17} cps/cm², or 5-10 ml of a 0.1 N solution relative to HNO_3 containing $\sim 10^{-5}$ mol/litre of ^{237}Np .

Reagents. The cation exchanger KU-2 in the H^+ form with a grain diameter of about 0.1 mm. NaNO_2 . 1 N solution of HNO_3 .

Performance of Work

Prepare in a test tube 5-10 ml of a 0.1 N solution relative to HNO_3 containing tracer amounts of ^{239}Np (10^4 cpm/ml) or ^{237}Np ($\sim 10^3$ cpm/ml). To obtain Np^{V} , heat the solution in the presence of NaNO_2 (0.1 M) on a water bath at 50-60 °C during 15 min. Dilute the prepared solution of Np^{V} up to a concentration of 0.05 N relative to HNO_3 and pass it through the chromatographic column filled with the resin KU-2 in the H^+ form. Next wash the column with 12-13 ml of 1 N HNO_3 at a rate of 0.2 ml/min (desorption of Np^{V}); gather the eluent in the form of individual small fractions in small beakers or test tubes for measuring the β -activity by fractions.

Plot a curve of the amount of Np^{V} (in %) against the number of column volumes of the eluent. Use this curve to determine the volume of the washing solution V_{max} corresponding to the peak of the elution curve. Evaluate the exchange constant by the formula:

$$K = \frac{V_{\text{max}} [\text{H}^+]^z}{a^z V}$$

where V_{max} is the volume of the washing solution (eluent) corresponding to the peak on the elution curve, ml, $[\text{H}^+]$ is the hydrogen ion concentration in the washing solution of acid, mequiv/ml, z is the charge of the ion being displaced

(in the given case $z = 1$), a is the total exchange capacity of the resin equal to 2.5 mequiv/ml, and V is the volume of the resin taken for the experiment, ml.

Experiment 14.7. COMPLEXING OF Np IN AQUEOUS SOLUTIONS [12-15]

The aim of any method of studying complexing in solutions is the determination of the composition (general formulas) of the complexes and their stability constants.

In studying the chemistry of complex compounds of the transuranium elements, the greatest favour has been given to physicochemical methods (spectrophotometry, ion exchange, extraction, polarography, and some others).

A. SYSTEM $\text{Np}^{\text{IV}}\text{-H}_2\text{C}_2\text{O}_4\text{-HCl}$

Equipment and Reagents

Equipment and Utensils. A counter with a scintillation or semiconductor detector of α -radiation. A centrifuge. A device for determining solubility. A water bath. A thermostat. A liquid proportioner. Quartz or glass test tubes for 20-25 ml (3). Glass rods. Conical flasks for 100-200 ml (3). A calibrated or capillary pipette for 2-5 ml.

Radioactive Substances. 5-10 ml of a solution, 1 N relative to HNO_3 , containing about 5×10^{-2} mol/litre of $^{237}\text{Np}^{\text{V}}$.

Reagents. $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$. $(\text{NH}_4\text{SO}_4)_2\text{Fe}$. Solutions: 0.5 N HCl ; mixed—1 N relative to HCl and 1×10^{-4} - 2×10^{-1} M $\text{H}_2\text{C}_2\text{O}_4$ (oxalic acid).

Performance of Work

Pour 5-10 ml of a 1 N solution relative to HNO_3 containing $\sim 5 \times 10^{-2}$ mol/litre of $^{237}\text{Np}^{\text{V}}$ into a quartz test tube. To obtain Np^{IV} , heat the solution in the presence of $\text{N}_2\text{H}_4 \times \text{HNO}_3$ (0.2-0.3 M) on the water bath at 70-80 $^\circ\text{C}$ during 30 min. After cooling the solution, add to it ~ 0.01 mol/litre of iron(II) sulphamate. Next obtain $\text{Np}(\text{C}_2\text{O}_4)_2 \cdot x\text{H}_2\text{O}$ by adding finely ground $\text{H}_2\text{C}_2\text{O}_4$ in small portions up to decolorization of the solution. Centrifuge the solution with the precipitate. After decanting the mother liquor, wash the precipitate two or three times with 0.5 N hydrochloric acid. Next pour an aqueous solution of oxalic acid of a definite concentration (1×10^{-4} to 2×10^{-1} M) in the presence of 1 N hydrochloric acid over the precipitate of $\text{Np}(\text{C}_2\text{O}_4)_2 \cdot x\text{H}_2\text{O}$.

Transfer the pulp into a vessel for determining the solubility (with a capacity of 20-30 ml) and stir the precipitate during 4-6 h in the thermostat at 20 °C. After settling of the precipitate, take samples (of 0.9 ml each) with the aid of the liquid proportioner for measuring the α -activity of the equilibrium solution. Perform the experiments at several values of the oxalic acid concentration.

Evaluate the stability constants of the oxalate complexes of the Np^{IV} with the aid of the "degree of complexing" function Φ equal to the ratio of the total concentration of the metal in the solution to the equilibrium concentration of the free ions of the metal:

$$\Phi = \frac{\sum [\text{Np}^{\text{IV}}]}{[\text{Np}^{4+}]}$$

In the given case, the total concentration of the Np^{IV} in the solution equals the solubility L of the salt in the indicated conditions, while the equilibrium concentration of the free neptunium ions is determined by the solubility product P_s of $\text{Np}(\text{C}_2\text{O}_4)_2 \cdot x\text{H}_2\text{O}$ equal to 5×10^{-22} divided by the equilibrium concentration of the ion $\text{C}_2\text{O}_4^{2-}$ evaluated by the equation

$$[\text{C}_2\text{O}_4^{2-}] = \frac{\sum [\text{H}_2\text{C}_2\text{O}_4]}{1 + ([\text{H}^+]/K_2 + [\text{H}^+]^2/K_1K_2)}$$

where $\sum [\text{H}_2\text{C}_2\text{O}_4]$ is the initial concentration of the oxalic acid in the solution, $[\text{H}^+] = 1 \text{ N}$, and K_1 and K_2 are the stepwise dissociation constants of the $\text{H}_2\text{C}_2\text{O}_4$.

The solubility of the $\text{Np}(\text{C}_2\text{O}_4)_2 \cdot x\text{H}_2\text{O}$ in the investigated solutions is

$$L = [\text{Np}^{4+}] + [\text{Np}(\text{C}_2\text{O}_4)^{2+}] + [\text{Np}(\text{C}_2\text{O}_4)_2] + [\text{Np}(\text{C}_2\text{O}_4)_3^-] + [\text{Np}(\text{C}_2\text{O}_4)_4^{1-}] \quad (14.2)$$

Using the expressions for the "degree of complexing" function Φ and the stability constant β_j , we obtain

$$\Phi = \sum_{j=1}^4 1 + \beta_j [\text{C}_2\text{O}_4^{2-}]^j \quad (14.3)$$

Hence we can obtain the functions:

$$\Psi_1 = \frac{\Phi - 1}{[\text{C}_2\text{O}_4^{2-}]} = \beta_1 + \beta_2 [\text{C}_2\text{O}_4^{2-}] + \beta_3 [\text{C}_2\text{O}_4^{2-}]^2 + \beta_4 [\text{C}_2\text{O}_4^{2-}]^3$$

$$\Psi_2 = \frac{\Psi_1 - \beta_1}{[\text{C}_2\text{O}_4^{2-}]} = \beta_2 + \beta_3 [\text{C}_2\text{O}_4^{2-}] + \beta_4 [\text{C}_2\text{O}_4^{2-}]^2 \quad (14.4)$$

$$\Psi_3 = \frac{\Psi_2 - \beta_2}{[C_2O_4^{2-}]} = \beta_3 + \beta_4 [C_2O_4^{2-}]$$

$$\Psi_4 = \frac{\Psi_3 - \beta_3}{[C_2O_4^{2-}]}$$

The functions Ψ_1 , Ψ_2 , Ψ_3 , and Ψ_4 at $[C_2O_4^{2-}] \rightarrow 0$ tend to the corresponding limiting values β_1 , β_2 , β_3 , and β_4 , i.e. by extrapolation of the straight line plotted in the coordinates Ψ against $[C_2O_4^{2-}]$ up to $[C_2O_4^{2-}] = 0$, we determine the values of the stability constants. Enter the obtained experimental and calculated data for determining β_j into a table according to the following example:

$\sum [H_2C_2O_4],$ mol/litre	L, mol/litre	$[C_2O_4^{2-}],$ mol/litre	$[Np^{4+}] = \frac{P_s}{[C_2O_4^{2-}]^2},$ mol/litre	Ψ_1	Ψ_2	Ψ_3	Ψ_4
0.003							
0.006							
0.012							
0.020							
0.200							
0.800							

After performing the experiment, combine the solutions containing ^{237}Np for regeneration by precipitation of the hydroxide.

B. SYSTEM $\text{NpV-}\alpha\text{-HYDROXYISOBUTYRIC ACID}$

Neptunium in solutions forms complexes of the composition $[\text{NpO}_2(o\text{-But})]^0$ and $[\text{NpO}_2(o\text{-But})_2]^-$ whose stability constants are determined by the spectrophotometric method. Here auxiliary functions are used from which the stability constants are obtained by extrapolation to the zero value of the variable.

Equipment and Reagents

Equipment and Utensils. A counter with a scintillation or semiconductor detector of α -radiation. A spectrophotometer (SF-4, SF-6). Quartz or glass planchets (2) with an absorbing layer 1 cm thick. An electronic potentiometer (LP-58, LPU-01, etc.) or a laboratory pH meter ("pH 673"). Glass test tubes for 10 ml (6). A capillary pipette for 2-3 ml. A calibrated micropipette with a syringe. Chemical beakers for 50-100 ml (5).

Radioactive Substances. 20-25 ml of a solution of 0.1-0.2 *N* relative to HNO_3 containing about 0.001 mol/litre of $^{237}\text{Np}^{\text{V}}$.

Reagents. NaClO_4 , α -hydroxyisobutyric acid. Dilute solutions of NH_4OH and HClO_4 .

Performance of Work

Prepare 4-5 ml of 0.5 *M* solutions relative to NaClO_4 containing $^{237}\text{Np}^{\text{V}}$ (8×10^{-4} *M*) and α -hydroxyisobutyric acid with a concentration varying from 0 to 0.2 *M* in each of five beakers. Add NaClO_4 to maintain a constant ionic strength (0.5). Also add NaNO_2 (~ 0.1 *M*) to the initial solutions to stabilize the Np^{V} . Determine the content of neptunium in the solution by the radiometric or spectrophotometric method.

Use the potentiometer or pH meter to establish the pH of the initial solutions at about 5.5 and keep it constant by adding a dilute solution of NH_4OH or HClO_4 dropwise. Transfer aliquot parts of the prepared solutions (3.0-3.5 ml) with the aid of the pipette into the quartz or glass planchets and measure the optical densities within the wavelength interval of 960-1010 nm. For calculations, next select the peak within the interval from 978 to 983 nm (absorption of the free ion NpO_2^+). From the values of D_{max} , subtract the magnitude of the background equal to $(D_{960} + D_{1010})/2$. Perform all the measurements of the optical density in comparison with the zero solution (containing no Np).

After measuring D_{max} for the series of solutions containing Np^{V} with a varying concentration of the α -hydroxyisobutyric acid on the background of a 0.5 *M* solution of NaClO_4 , calculate (according to K. Yatsimirsky's method) the relevant stability constants for the complexes $[\text{NpO}_2(o\text{-But})]^0$ and $[\text{NpO}_2(o\text{-But})_2]^-$.

For this purpose, first use the generally known expression

$$\Delta \bar{\epsilon} = \frac{\Delta \epsilon_1 \beta_1 [A] + \Delta \epsilon_2 \beta_2 [A]^2}{1 + \beta_1 [A] + \beta_2 [A]^2}$$

by means of which we find the auxiliary functions

$$f_1 = \frac{\Delta\bar{\varepsilon}}{[A]} \quad \text{and} \quad f_2 = \frac{f_1 - a_1}{[A]}$$

By extrapolation of the curves of these functions to a zero concentration of the ligand $[A]$, we determine the limiting values:

$$\begin{aligned} \lim f_1 &= a_1 = \Delta\varepsilon_1\beta_1 \quad \text{and} \quad \lim f_2 = a_2 \\ &= \Delta\varepsilon_2\beta_2 - \Delta\varepsilon_1\beta_1^2 \end{aligned}$$

Next, using the new variable $y = 1/[A]$, we obtain the following equation:

$$\Delta\bar{\varepsilon} = \frac{\Delta\varepsilon_2\beta_2 + \Delta\varepsilon_1\beta_1 y}{\beta_2 + \beta_1 y}$$

By extrapolation of $\Delta\bar{\varepsilon}$ to the zero value of y , we find

$$\lim \Delta\bar{\varepsilon} = b_1 = \Delta\varepsilon_2$$

Upon the extrapolation to $y \rightarrow 0$ of another auxiliary function

$$\varphi_1 = (\sim\Delta\bar{\varepsilon} - b_1)/y,$$

we obtain

$$\lim \varphi_1 = b_2 = (\Delta\varepsilon_1 - \Delta\varepsilon_2) \frac{\beta_1}{\beta_2}$$

Hence by solving the system of found equations, we calculate the values of the constants and molar coefficients of absorption:

$$\beta_1 = \frac{a_1 b_1 - a_2 b_2}{a_1 b_2 + b_1^2} \quad \text{and} \quad \beta_2 = \frac{a_1^2 + a_2 b_1}{a_1 b_2 + b_1^2}$$

$$\Delta\varepsilon_1 = \varepsilon_1 - \varepsilon_M = \frac{a_1^2 b_2 + a_1 b_1^2}{a_1 b_1 - a_2 b_2}$$

and

$$\Delta\varepsilon_2 = \varepsilon_2 - \varepsilon_M = b_1$$

By comparing the values of $\Delta\varepsilon_{\text{calc}}$ and $\Delta\varepsilon_{\text{exper}}$, which should virtually coincide, arrive at conclusions on the authenticity of the performed calculations of the constants.

Enter the results of your calculations into a table of the following form:

No.	[o-But-], mol/litre	D _{97%}	$\bar{\epsilon}$	$\Delta\epsilon_{\text{exper}}$	f_1	f_2	ν	φ_1	$\Delta\epsilon_{\text{calc}}^{***}$	β_1	β_2
1	0.01										
2	0.05										
3	0.10										
4	0.15										
5	0.20										
6	0.25										

* Calculate by the equation: $[\text{o-But-}] = \frac{\sum [\text{HL}]}{1 + (\text{H}^+/\text{K}_{\text{dis}})}$, where $\text{K}_{\text{dis}} = 1.5 \times 10^{-4}$ is the dissociation constant of α -hydroxyisobutyric acid at $\mu = 0.5$.
 ** Calculate by introducing β_1 and β_2 into K. Yatsimirsky's equation.

Upon completing the experiment, combine the working solutions containing ^{237}Np for regeneration by precipitation of the hydroxide.

C. SYSTEM NpV-LACTIC ACID

The chemistry of complex compounds of Np^{V} has been studied the most completely by the method of ion exchange. To determine the composition and stability constants, it is necessary to find the values of the distribution coefficients of Np^{V} between the cation exchanger and the solutions of the complexing agent in the chosen conditions of an experiment.

Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window counter. An electronic potentiometer (LP-58, LPU-01, etc.) or a laboratory pH meter ("pH 673"). A shaker. A liquid proportioner. A water bath. A test tube for 10 ml. Flasks or test tubes for 50 ml (10). A capillary pipette for 2-5 ml. A calibrated pipette with a syringe. A glass burette for 25 ml.

Radioactive Substances. 1-2 ml of a 1 N solution relative to HNO_3 containing ^{239}Np with a specific activity of about 10^6 cpm/ml.

Reagents. NaNO_3 . NH_4ClO_4 . Na_2CO_3 . $(\text{NH}_4)_2\text{HPO}_4$. Lactic acid. Cation exchanger KU-2 in the NH_4^+ form (grain size 50-70 mesh). Solutions: 1 N HNO_3 ; 0.1 N HClO_4 ; 0.1 N NH_4OH ; 0.15 and 0.2 M NH_4ClO_4 .

Performance of-Work

Prepare 1-2 ml of a 1 *N* solution relative to HNO₃ containing tracer amounts of ²³⁹Np (~10⁶ cpm/ml) in a test tube. To stabilize the Np^V, heat the solution in the presence of NaNO₂ (~0.1 *M*) on the water bath at 50-60 °C during 15 min. Next prepare a series of solutions of varying concentration relative to the complexing agent:

(1) 0.15 *M* relative to NH₄ClO₄ and containing Na₂CO₃ within the interval of 0.005-0.07 *M*; pH = 8.0;

(2) 0.2 *M* relative to NH₄ClO₄ and containing (NH₄)₂HPO₄ within the interval of 0.005-0.05 *M*; pH = 6.5;

(3) 0.2 *M* relative to NH₄ClO₄ and containing lactic acid within the interval of 0.005-0.15 *M*, pH = 6.5.

Also prepare solutions of 0.15 and 0.2 *M* relative to NH₄ClO₄ without a complexing agent, pH = 6.5 and 8.0.

Transfer 12.5 ml from each prepared solution into a flask or test tube (with a volume of about 50 ml), add to each of them 250 mg of the resin KU-2 in the NH₄⁺ form and 0.1 ml of the initial solution containing Np^V. After this establish the required pH of the solution (8.0 or 6.5) by adding dilute (~0.1 *N*) solutions of HClO₄ and NH₄OH; control the pH with the aid of the potentiometer or pH meter with a glass electrode. Vigorously stir the mixtures in a shaker during 4-6 h at room temperature. Separate the resin by filtration or by simply letting the solution settle, measure the β-activity of the unsorbed Np^V and evaluate the distribution coefficients *K*_d of the Np^V depending on the concentration of the complexing agent anion in the solution.

Take the value of *K*_d⁰ equal to the distribution coefficient of Np^V in the absence of the complexing agent in the solution.

The composition and stability constants of the complexes can be determined according to the methods of Schubert and Froneus (see p. 202), or according to that of V. Paramonova:

$$\frac{1-v_+}{v_+} = \beta_1 [A] + \beta_2 [A]^2$$

Here

$$v_+ = \frac{(100 - [M]) [M]_0}{(100 - [M_0]) [M]}$$

where [M]₀ and [M] are the equilibrium concentration of the metal-containing ion in the solution in the absence and in the presence of the complexing agent, respectively, %.

The total amount of the element being studied in the initial solution is 100%. Determine the equilibrium concentration of the complexing ligand [A] by the equations:

$$[\text{HPO}_4^{2-}] = \frac{\sum [\text{H}_3\text{PO}_4]}{1 + ([\text{H}^+]/K_2) + ([\text{H}^+]^2/K_1K_2) + (K_3/[\text{H}^+])}$$

and

$$[\text{Lact}^-] = \frac{\sum [\text{HLact}]}{1 + ([\text{H}^+]/K_{\text{diss}})}$$

The dissociation constants of the relevant acids are given in the literature, while the equilibrium concentration of the hydrogen ions is determined by the value of the pH of the system being studied. Use the found stability constants to calculate the concentrations of the separate complex forms of Np^{V} ; here $[\text{NpO}_2^+] = (K_d/K_d^0) [\text{M}]$. Enter the results of the calculations in a common table.

Experiment 14.8. PREPARATION OF SOME SIMPLE AND COMPLEX COMPOUNDS OF Np [2, 12]

Neptunium compounds are prepared, as a rule, by the conventional methods of inorganic synthesis.

The experiment is performed in a laboratory of class III in a sealed fume cupboard or a glove box.

Equipment and Reagents

Equipment and Utensils. A counter with a scintillation detector of α -radiation. A liquid proportioner. A centrifuge. A water bath. A transparent thermoplastic (Plexiglas) stand with openings for test tubes. Glass test tubes for 10 ml (10). A capillary pipette for 2-5 ml. Conical and measuring flasks for 50-100 ml (4). Glass rods.

Radioactive Substances. A 2 N solution (~ 5 ml) relative to HNO_3 containing 4.4×10^{-2} - 6.6×10^{-2} mol/litre of $^{237}\text{Np}^{\text{V}}$.

Reagents. $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$. $(\text{NH}_4\text{SO}_4)_2\text{Fe}$. NaNO_2 . KMnO_4 . KBrO_3 . Solutions: 1 N and concentrated HNO_3 ; concentrated NH_4OH ; 2 N NaOH ; 2 N KOH .

Performance of Work

(a) Preparation of Hydroxides

Prepare consecutively in each of three test tubes 4-5 ml of a 1 N solution relative to HNO_3 containing 10-15 mg of neptunium in the oxidation state +4, +5, and +6 as

described in Experiment 14.1. Add concentrated ammonium hydroxide or a 2 *N* solution of NaOH to these solutions dropwise while stirring with a glass rod up to a pH above 10. Observe the precipitation of neptunium hydroxides in various oxidation states, their form (amorphous or crystalline), and colour.

*(b) Preparation of Oxalate of Np^{IV}
and Peroxide of Np^{IV}*

Prepare 4-5 ml of a 1 *N* solution relative to HNO₃ containing 4.0×10^{-2} - 6.0×10^{-2} mol/litre of ²³⁷Np^{IV} in each of two test tubes. Add oxalic acid (~0.1 *M*) to the solution in one test tube while stirring with a glass rod. Observe the precipitation of Np(C₂O₄)₂·6H₂O, its form (amorphous or crystalline), and colour. Add a 5 *M* solution of H₂O₂ in small portions to the contents of the other tube while mixing with a glass rod up to complete decolourization of the solution. Observe the precipitation of the peroxide of Np^{IV}, its form (amorphous or crystalline) and colour. In a similar way prepare a precipitate of the oxalate of Np^{VI}.

(c) Preparation of Sodium Neptunyltriacetate

Prepare 2-3 ml of a solution of the composition: 0.02 *M* relative to Np^{VI}, 0.15 *M* relative to KBrO₃, and 0.3 *N* relative to H₂SO₄ in a test tube. Neptunium in the +6 oxidation state is prepared by heating the solution on the water bath at 80-90 °C during two hours. After cooling the solution, add to it while stirring an equal volume of a solution, 4 *M* relative to CH₃COONa and 4 *M* relative to NaNO₃. Observe the formation of a precipitate of NaNpO₂ × (CH₃COO)₃, its form (amorphous or crystalline), and colour.

(d) Preparation of Compounds of Np^{VII}

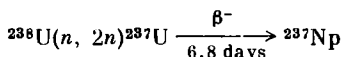
Prepare 4-5 ml of a 0.5-1 *N* solution relative to NaOH containing 15-20 mg of ²³⁷Np^{VII} in each of two test tubes as described in Experiment 14.1. Slowly add 0.1-0.2 *M* Ba(NO₃)₂ to the solution in one tube while stirring so that the barium content in the mother liquor does not exceed the solubility of the Ba(OH)₂ in the given conditions. Observe the precipitation of Ba₃(NpO₅)₂·*n*H₂O, its form (amorphous

or crystalline), and colour. Prepare the compound $\text{Sr}_3(\text{NpO}_5)_2 \times n\text{H}_2\text{O}$ in the other tube in a similar way, the only difference being that $\text{Sr}(\text{NO}_3)_2$ is used as the precipitant.

Prepare 4-5 ml of a 0.5-1 *N* solution relative to KOH containing 15-20 mg of $^{237}\text{Np}^{\text{VII}}$ in a third test tube. Slowly add aqueous 0.01-0.02 *M* $[\text{Co}(\text{NH}_3)_6\text{Cl}_3]$ to the solution with stirring. Observe the precipitation of $[\text{Co}(\text{NH}_3)_6]\text{NpO}_5 \times 3\text{H}_2\text{O}$, its form (amorphous or crystalline), and colour.

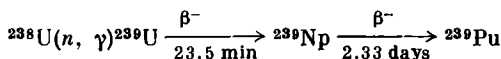
Experiment 14.9. SEPARATION OF ^{239}Np FROM URANIUM IRRADIATED BY NEUTRONS [11, 13]

The long-lived neptunium isotope ^{237}Np forms as a by-product in the operation of a uranium nuclear reactor:



Neptunium-237 is an α -emitter with $T_{1/2} = 2.2 \times 10^6$ years and a radiation energy of 4.77 MeV.

When ^{238}U is irradiated by slow neutrons, ^{239}Np is obtained with an energy of its β^- -radiation of 0.718 MeV:



Uranyl nitrate hexahydrate, uranium dioxide, and uranous-uranic oxide are convenient chemical forms of a uranium target for obtaining ^{239}Np because apart from uranium they contain no strongly activating elements.

When about 50 mg of uranium dioxide are irradiated, for example, in a nuclear reactor with a neutron flux density of 8×10^{12} cps/cm² during one day, about 150 MBq (4 mCi) of ^{239}Np accumulates in the target by the end of the irradiation; the γ -activity of the target at the end of irradiation is about 150 mequiv of Ra, while in two days after the end of irradiation, it is about 50 mequiv of Ra. This is why the target after irradiation is usually left standing for one or two days for decay of the short-lived fission products ("de-excitation"), and only then is the ^{239}Np separated. The radiochemical purity of the ^{239}Np is monitored by measuring the β, γ -spectra and determining $T_{1/2}$ or λ .

Neptunium is usually separated from irradiated uranium by methods of coprecipitation, extraction, and ion exchange.

Here oxidation-reduction reactions and processes of formation of simple and complex compounds of the elements being separated in aqueous solutions are used. These methods are based on the possibility of obtaining uranium, neptunium, and plutonium in different oxidation states in the same solution, and on the difference in the behaviour of these elements in coprecipitation, ion exchange, and extraction.

All the work involved in separating ^{239}Np from irradiated uranium is performed in a glove box of type 2-UKZ, 2-KZ (class I laboratory) or in a stainless steel fume cupboard (class II laboratory) with the use of a lead screen 5-8 cm thick.

A. ACETATE-SULPHATE METHOD OF COPRECIPITATION

Neptunium can be separated from irradiated uranium by coprecipitating it in the oxidation state $+4$ or $+6$. In the sodium uranylacetate method, the property of Np^{VI} to coprecipitate with $\text{NaUO}_2(\text{CH}_3\text{COO})_3$ is used. The coprecipitation of Np^{IV} is used in the most widespread lanthanum fluoride cycle, and also in the zirconium phosphate, sulphate, and phenyl arsonate methods.

Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window counter. A nuclear reactor with a neutron flux density of $\sim 10^{12}$ cps/cm² or a laboratory source of neutrons with an intensity of 10^6 - 10^8 neutron/s. A water bath. A centrifuge. A laboratory container (KL-7) with a shielding wall having a thickness (over the lead) of 70 mm. An aluminium container with a screwing on lid, 60 mm high and with an external diameter of 38 mm. Collecting containers: for liquid radioactive wastes with a shielding wall having a thickness (over the lead) of 20-30 mm and for solid radioactive waste (KS-G). Chemical beakers for 100 ml (3-5). Capillary pipettes: for 5-10 ml (2) and for 1 ml (paraffin-coated). Glass rods. Conical flasks for 250 ml (4). Glass and polyethylene test tubes for 5-10 ml (5).

Radioactive Substances. 50 mg of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ irradiated by a flux of neutrons during a period of time sufficient for the accumulation of ~ 40 MBq (1 mCi) of ^{239}Np (calculate the yield of the formed ^{239}Np as described in Chap. 8, Vol. 1).

Reagents. $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. 1 N solution of HNO_3 . $\text{La}(\text{NO}_3)_3$. $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$. Solutions: 3% KMnO_4 , saturated CH_3COONa and K_2SO_4 ; concentrated H_2SO_4 ; 2 N HNO_3 .

Performance of Work

The method is based on the coprecipitation of Np^{VI} with sodium uranyltriacetate in the presence of an oxidizing agent (KMnO_4). In the first stage of separation, the neptunium is separated from the main mass of the fission fragments; in the next stage of purification, it is separated from the uranium in the presence of a reducing agent by the coprecipitation of Np^{IV} with $\text{K}_3\text{La}(\text{SO}_4)_3$. The Np^{VI} is reduced to Np^{IV} using a 0.1 M solution of $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$ with heating of the solution.

Irradiate ~ 50 mg of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}^*$ with a flux of neutrons in a quartz test tube with a ground-glass stopper during the time needed for the accumulation of ~ 40 MBq (1 mCi) of ^{239}Np . Put the sample contained in the quartz test tube with the ground-glass stopper into the aluminium container with the screwing on lid. After "de-excitation" during one or two days, deliver the laboratory container to the glove box or fume cupboard, then directly at the place of work behind the lead shielding screen extract the aluminium container from the laboratory one, and take out of it the test tube with the irradiated $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Use very simple tongs, for instance remote pincers with notches or jaws on its ends.

Dissolve the uranium sample in the test tube in 3-5 ml of hot 1 N nitric acid containing a few drops of a 3% solution of KMnO_4 for oxidizing the neptunium to an oxidation state of +6. Heat the solution in the test tube on the water bath at 80-90 °C during 10-15 min; if MnO_2 precipitates, separate it by filtration or centrifuging. Next add to the solution an equal volume of a saturated solution of CH_3COONa in small portions with stirring. Stir the formed precipitate of sodium uranyltriacetate with a glass rod, let it settle for 30 min, after which centrifuge the precipitate and wash it twice with a saturated solution of CH_3COONa . Pour the highly active decanted and washing liquids into the collecting container for liquid radioactive wastes having a wall thickness (lead) ensuring the required shielding from radiation, and hand it in for disposal. (*Handle with care, a high radioactivity!*).

* A different amount of the irradiated material may be taken depending on the density of the neutron flux from the source and on the duration of irradiation.

Dissolve the precipitate in 2 ml of concentrated sulphuric acid containing hydrazine ($\sim 0.1 M$) and heat the solution during 20 min to reduce the Np^{VI} to Np^{IV} .

To precipitate $\text{K}_2\text{La}(\text{SO}_4)_3$, add to the solution 3 ml of a saturated solution of K_2SO_4 and a solution of $\text{La}(\text{NO}_3)_3$ up to a concentration (reduced to La) of 1 ml per ml of solution. Let the precipitate settle for 30 min, centrifuge it, wash it twice with a saturated solution of K_2SO_4 and dissolve it in a minimum volume of 2 N nitric acid. The final solution containing ^{239}Np also contains macroamounts of K^+ , La^{3+} , NO_3^- , and SO_4^{2-} .

Check the radiochemical purity of the separated ^{239}Np according to its half-life; to do this, measure in time the β -activity of an aliquot part of the final solution by the radiometric method. Plot a decay curve in semilogarithmic coordinates and find the half-life of the ^{239}Np . Also evaluate the decay constant and the half-life by the method of least squares.

Immediately use the solution containing the ^{239}Np for performing a radiochemical experiment.

B. EXTRACTION METHOD

Among the extraction methods of separation, the most convenient is the one based on the selective extraction of Np^{VI} with diethyl ether from nitric acid solutions in the presence of a salting out agent— $\text{Ca}(\text{NO}_3)_2$ and the different extraction] behaviour of Np^{VI} and Np^{V} . The extraction is performed on the background of the oxidizing agents NaBiO_3 or KBrO_3 .

Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window counter. A nuclear reactor with a neutron flux of $\sim 10^{12}$ cps/cm² or a laboratory source of neutrons with an intensity of 10^5 – 10^8 neutron/s. A water bath. A laboratory container (KL-7) with a thickness of the shielding wall (over lead) of 70 mm. An aluminium container with a screwing on lid 60 mm high with an external diameter of 38 mm. A collecting container for liquid radioactive wastes with a shielding wall thickness (over lead) of 20–30 mm. Chemical beakers for 100 ml (3). Separatory funnels for 500 ml (3). A watch glass. Glass rods. Capillary pipettes for 3–5 ml (2).

Radioactive Substances. About 50 mg of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ irradiated with a flux of neutrons during the time needed for the accumulation of ~ 40 MBq (1 mCi) of ^{239}Np .

Reagents. $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. Diethyl ether. Zirconium nitrate. $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$. Solutions: 1 *N* and 4 *M* HNO_3 , 0.15 *M* KBrO_3 .

Performance of Work

Irradiate ~ 50 mg of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ by a flux of neutrons in a quartz test tube with a ground-glass stopper during a time sufficient for accumulating ~ 40 MBq (1 mCi) of ^{239}Np and determined by calculation. After de-excitation of the sample for about two days, deliver the laboratory container to the working premises. Extract the $\text{UO}_2(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ from the aluminium container with pincers, transfer it into a 100-ml chemical beaker, and dissolve it in 3 ml of hot 4 *M* nitric acid. Next add 10 ml of an 0.15 *M* solution of KBrO_3 to the solution, cover the beaker with the watch glass, and heat the solution during 15-20 min on the water bath without letting it boil. Introduce 29 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ into the beaker with the hot solution and dissolve it, after which cool the solution and transfer it into a 500-ml separatory funnel. Extract the Np^{VI} with diethyl ether (70 ml) with vigorous shaking during one or two minutes behind the lead screen 70-80 mm thick. (In addition to other means of individual protection, be sure to use plastic oversleeves or gloves 2-3 mm thick with long sleeves.)

After settling for 10 minutes, separate the aqueous phase and pour it into the collecting container for liquid radioactive wastes. (*Handle with care, a high radioactivity!*).

Transfer the extract into another separatory funnel and wash it twice with half volumes of a solution of 4.3 *M* relative to $\text{Ca}(\text{NO}_3)_2$ and 0.4 *N* relative to HNO_3 containing about 0.5 g of NaBiO_3 and 0.4 g of zirconium nitrate (basic) per 100 ml of the solution. Reextract the neptunium-239 from the organic phase with two volumes (100 ml each) of a solution of 3.3 *M* relative to $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 1 *N* relative to HNO_3 , and 0.1 *M* relative to $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$. Add 11 ml of 1 *N* HNO_3 to the combined aqueous extracts and introduce a finely ground powder of NaBiO_3 in small portions with stirring up to complete oxidation of the hydrazine; the solution acquires a non-vanishing brown colour because of the surplus of the NaBiO_3 suspension. Add 29 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ to the solution, transfer the resulting solution into a clean separatory funnel and reextract

the Np^{VI} with 70 ml of ether. Pour off the aqueous phase into the collecting container for liquid radioactive wastes, and wash out the neptunium compounds from the organic phase with 20 ml of distilled water.

Monitor the radiochemical purity of the separated ^{239}Np according to its half-life. Immediately use the final solution containing ^{239}Np for performing a radiochemical experiment.

C. CHROMATOGRAPHIC METHOD

In the method of cation-exchange chromatography, the +5 oxidation state of neptunium is especially convenient for separating U, Np, and Pu. This is due, first, to the high stability of Np^{V} and to the possibility of its existing in one solution with U^{VI} and Pu^{IV} , and, second, to the fact that NpO_2^+ is retained on cation exchangers much more weakly than the ions UO_2^{2+} , Pu^{4+} , and the ions of most of the fission products. The Np^{V} is eluted from the cation exchanger with a 1 *N* solution of HNO_3 much earlier than the U^{VI} , while the main part of the fission products is not eluted by nitric acid. Some of the fission products, however, (Ru, Te, I, etc.) can be detected in the neptunium fraction. This is why radiochemically pure ^{239}Np is obtained only upon the following extraction with ether.

Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window counter. A nuclear reactor with a neutron flux density of 10^{12} – 10^{13} cps/cm² or a laboratory source of neutrons with an intensity of 10^5 – 10^8 neutron/s. Chromatographic columns 35 cm long and 0.5 cm in diameter (3). A water bath. A laboratory container (KL-7) with a thickness of the shielding wall (over lead) of 70 mm. An aluminium container with a screwing on lid 60 mm high and having an external diameter of 38 mm. Collecting containers for solid and liquid radioactive wastes (KS-G) with a shielding wall thickness (over lead) of 20–30 mm. A quartz test tube. A separatory funnel for 500 ml. Chemical beakers for 100 ml (3).

Radioactive Substances. About 50 ml of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ irradiated by a flux of neutrons during the time needed for accumulating 40 MBq (1 mCi) of ^{239}Np .

Reagents. Diethyl ether. Cation exchanger KU-2 in the H^+ form with a grain diameter of ~ 0.1 mm. Solutions: 1 *N* and 4 *M* HNO_3 ; saturated KBrO_3 .

Performance of Work

Irradiate about 50 mg of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in a quartz test tube with a ground-glass stopper during the time needed for the accumulation of 40 MBq (1 mCi) of ^{239}Np and determined by calculation (see Vol. 1, p. 233). After de-excitation of the specimen for about two days, deliver the laboratory container to the working premises. Extract the $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ from the aluminium container with the aid of pincers, transfer it into a 100-ml chemical beaker, and dissolve in a minimum volume of hot 4 *M* nitric acid.

Dilute the obtained solution with distilled water up to 1 *N* relative to HNO_3 . The neptunium is evidently in the form of Np^{V} and Np^{VI} in this solution.

Transfer the solution into a chromatographic column prepared for operation and containing the cation exchanger KU-2. Next elute it with 13 ml of 1 *N* nitric acid at a rate of 0.2 ml/min. In this operation, the cation exchanger KU-2 reduces tracer amounts of Np^{VI} to Np^{V} . Add 2-3 ml of a saturated solution of KBrO_3 to the eluate in a 100-ml chemical beaker, heat the solution on the water bath during 15 min at 90 °C, after which saturate it with $\text{Ca}(\text{NO}_3)_2$ and treat it three times in the separatory funnel with diethyl ether (using portions equal to the volume of the solution). Combine the ether fractions, and reextract the neptunium from them with 1 *N* nitric acid while shaking during 1-2 min.

Remove the ether from the organic phase by evaporation, and put the remaining dry residue into the collecting container for radioactive wastes.

To obtain Np^{V} without contaminants, pass the obtained nitric acid solution of Np^{VI} through a small column with a cation exchanger and elute the neptunium with a small volume of 1 *N* HNO_3 .

After completing work, put the chromatographic columns with the resin into a lead beaker or a collecting container for radioactive wastes.

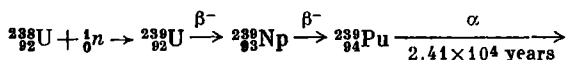
Determine the radiochemical purity of the separated ^{239}Np according to its half-life. Immediately use the solution containing ^{239}Np for performing radiochemical experiments with this isotope.

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Chapter 15 The Chemistry of Plutonium [1-4]

The long-lived radioactive isotope ^{239}Pu , which is the most convenient for studying plutonium, is obtained in large amounts in industrial nuclear reactors:



The radiometric, colorimetric, spectrophotometric, titrimetric, and electrochemical methods are used for the quantitative determination of plutonium. The most selective

and simple method of analysis is the radiometric one, which for this reason has found the greatest application.

The plutonium content is usually determined radiometrically as follows. An aliquot part V_1 of the solution being analysed (0.1-1.0 ml) is diluted with 1.0-1.5 *N* nitric acid in a measuring flask up to a definite volume V_2 (to avoid the obtaining of thick layers on the target). After the solution has been vigorously stirred by shaking it, a sample is taken (0.09-0.18 ml) with the aid of a calibrated pipette with a syringe or a liquid proportioner and is transferred onto a stainless steel disk. The latter (about 17 mm in diameter) has small sides that are lubricated with a special varnish (a solution of 4 g of polystyrene and 1.1 g of paraffin in 50 g of benzene). The solution on the disk is evaporated until dry with the aid of an infrared lamp (at a distance of 25-30 cm to avoid boiling and splashing out), after which the disk on a special stainless steel support is roasted on an electric stove up to complete burning out of the varnish. Here the volatile salts (for example, NH_4Cl and NH_4NO_3) contained in the solution are also removed.

The activity is measured in a scintillation counter. The plutonium content in the solution being analysed is determined by the formula

$$m_{\text{Pu}} = \frac{IVV_2 \times 100}{V_1 V_3 \varphi S} \quad (15.1)$$

where m_{Pu} is the mass of the plutonium in the initial solution being analysed, mg/ml, I is the measured α -activity of the sample, cpm, V is the total volume of the solution being analysed from which an aliquot part is taken, ml, V_1 is the volume of the aliquot part, ml, V_2 is the volume of the solution obtained after dilution with nitric acid, ml, V_3 is the volume of the solution transferred onto the disk, ml, φ is the counting coefficient of the registering installation determined with the aid of a standard preparation, %, and S is the specific activity of plutonium of the given isotopic composition, dpm/mg.

Experiment 15.1. OXIDATION-REDUCTION REACTIONS OF Pu IN SOLUTIONS [3, 4]

The process of oxidation of Pu^{III} or reduction of Pu^{IV} is attended by the transfer of one electron, therefore it occurs readily under the influence of single-electron oxidizing

or reducing agents. The same can be said about the oxidation of Pu^{V} or the reduction of Pu^{VI} .

The oxidation of Pu^{IV} to Pu^{V} (and the reverse process) proceeds much more difficultly. What happens here is the formation or destruction of a metal-oxygen bond, hence the process usually goes on very slowly.

The task of obtaining plutonium in a certain oxidation state consists in preparation of the initial solution containing ^{239}Pu , the performance of an oxidation-reduction reaction in definite conditions (composition, reagent, temperature, etc.), and in determination of its completeness and rate.

The oxidation states of plutonium are identified and their concentrations determined by measuring the electron absorption spectra (using spectrophotometers SF-4 and SF-6 with a slit width of 0.04 mm, SF-11 with a slit width of 0.01 mm, etc.). It must be borne in mind here that the discrepancy in the position of the absorption peaks of Pu-containing ions in solutions observed in some cases is due, in addition to other factors, to errors in instrument adjustment.

The plutonium content in a definite oxidation state is determined with the aid of calibration curves showing the optical density D_{max} at the given wavelength λ against the plutonium concentration c_{Pu} in the given oxidation state. Particularly, the curves shown in Fig. 15.1 can be used to determine Pu^{III} and Pu^{IV} jointly present in solutions. The plutonium content in various oxidation states is determined by what is called the method of differential spectrophotometry or the method of consecutive approximations.

Plutonium in various oxidation states is stabilized in different media (HNO_3 , HCl , HClO_4). This is why it is essential not only to have a high purity of the initial solutions, but also to use a special procedure for their dilution: the calibration solutions must be of the same normality relative to the HNO_3 (HCl , HClO_4) as the mixture being analysed. In obtaining calibration curves, it is customary practice to use absorption peaks for the different oxidation states near the following wavelengths:

$\text{Pu}^{\text{III}}-\lambda = 600-605 \text{ nm}$: a 1.0 *N* solution relative to HNO_3 is prepared containing 0.025 mol/litre of Pu^{III} ; a series of solutions of various concentrations is obtained by dilution with 0.5 *N* nitric acid.

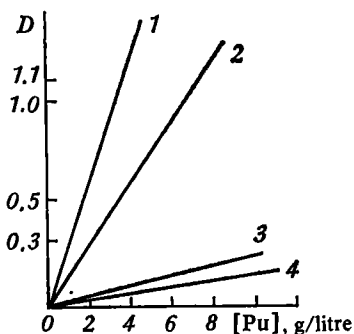


Fig. 15.1. Calibration curves for determining the concentration of Pu^{III} and Pu^{IV} by differential spectrophotometry:

1— Pu^{IV} at 476 nm; 2— Pu^{III} at 565 nm; 3— Pu^{IV} at 565 nm;
4— Pu^{III} at 476 nm

$\text{Pu}^{\text{IV}}-\lambda = 470-476 \text{ nm}$: the hydroxide $\text{Pu}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ is prepared; it is partly dissolved in 12 *M* nitric acid: at a ratio of the volumes of the HNO_3 and $\text{Pu}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ equal to 1:1, a 3 *M* solution relative to HNO_3 is obtained containing about 0.075 mol/litre of Pu^{IV} (the exact concentration is established separately); the completeness of oxidation of Pu^{III} to Pu^{IV} is checked, an aliquot part of the solution (0.2-0.3 ml) is diluted to 1 *N* relative to HNO_3 , is transferred into a glass or quartz planchet, and the spectrum of the solution is measured at wavelengths of 475-476, 560-565, and 600-605 nm: a sharp peak at 475-476 nm and the absence of absorption bands at 560-565 and 600-605 nm indicate that only Pu^{IV} is present in the solution; a series of solutions of various concentrations is obtained by diluting the solution with 0.05-0.1 *N* nitric acid.

$\text{Pu}^{\text{VI}}-\lambda = 831 \text{ nm}$: the initial solution is prepared (see Sec. E); dilution is performed in the same way as for Pu^{III} and Pu^{IV} .

$\text{Pu}^{\text{V}}-\lambda = 568-569 \text{ nm}$: prepare the initial solution (see Sec. D); dilute it with an 0.1 *N* (or less) solution of HClO_4 or HNO_3 .

To appraise the plutonium content in various oxidation states in a solution, one may sometimes use the well-known

Bouguer-Lambert-Beer relation:

$$c = \frac{D}{\epsilon_m d}$$

where c is the concentration, D is the optical density, ϵ_m is the molar absorption coefficient, and d is the thickness of the absorbing layer.

The experiment is run in a class II laboratory with the use of sealed fume cupboards or glove boxes.

A. PREPARATION OF Pu^{III}

Aqueous solutions of HClO₄, HCl, and HNO₃ containing Pu^{III} in the form of the ion Pu³⁺ have a light blue colour.

Plutonium(III) is prepared by reducing Pu^{IV} with the use of reducing agents such as hydroquinone, H₂ on smooth platinum or platinum black, hydrazine, hydroxylamine, SO₂, formaldehyde sodium sulfoxylate, Fe²⁺, Zn, SnCl₂, and H₂S. The strongest reducing agents for preparing Pu^{III} by the reaction Pu^{IV} → Pu^{III} are zinc amalgam, hydroquinone, and rongalite (the technical name of formaldehyde sodium sulfoxylate), which rapidly reduce Pu^{IV} at room temperature.

Equipment and Reagents

Equipment and Utensils. A spectrophotometer (SF-4, SF-8, SF-16, etc.). Rectangular quartz or glass planchets (2) with an absorbing layer 1 cm thick. A liquid proportioner. A water bath. A centrifuge. Glass test tubes for 10 ml (4). A capillary pipette for 2-5 ml. Conical flasks for 50-100 ml (4). Foil of platinized platinum. A glass capillary tube.

Radioactive Substances. A 1 *N* solution relative to HNO₃ containing 0.1 mol/litre of Pu^{IV}.

Reagents. Rongalite (or its saturated solution). N₂H₄·HNO₃. NH₂OH·HCl. Solutions: 1 *N* HNO₃.

Performance of Work

Add 10-15 mg/ml of formaldehyde sodium sulfoxylate (rongalite) to a test tube containing 3-4 ml of a 1 *N* solution relative to HNO₃ with 0.01 mol/litre of Pu^{IV} while stirring. Visually observe the change in the solution's colour.

Next transfer the solution into the quartz or glass planchet with the capillary pipette and measure its optical density

at 600-605 nm. Use the calibration curve in the coordinates $D_{\max}$ against $c_{\text{Pu}^{\text{III}}}$ to appraise the degree of reduction of the Pu^{IV} depending on the time elapsed from the instant of adding the reducing agent to the initial solution. Determine whether the reaction is slow, fast, or instantaneous.

Repeat the optical density measurements in different time intervals from the instant of preparing the solution (1, 2, 4 h, etc.); arrive at conclusions on the stability of Pu^{III} to oxidation by the oxygen of the air. In a similar way, prepare Pu^{III} with the aid of hydrazine and hydroxylamine added to the initial Pu^{IV} solution up to a concentration of 0.2-0.3 *M*. When using hydrazine, heat the solution on the water bath at 70-80 °C during 30 min.

B. PREPARATION OF Pu^{IV}

In aqueous solutions that are 0.3 *N* relative to H^+ (and higher), Pu^{IV} exists in the form of unhydrolyzed Pu^{4+}

Table 15.1. Oxidation-Reduction Reactions of Plutonium Ions in Preparing Pu^{IV} [2, 3]* (at Room Temperature)

Reaction	Reagents	Solution
$\text{Pu}^{\text{III}} \rightarrow \text{Pu}^{\text{IV}}$	BrO_3^-	Dilute acid
	$\text{Cr}_2\text{O}_7^{2-}$	Ditto
	MnO_4^-	Ditto
	HIO_3	Ditto
	Ce^{4+}	1.5 <i>N</i> relative to HCl containing 0.02 mol/litre of Pu^{III}
	H_2O_2 (0.2-0.5 <i>M</i>)	2 <i>N</i> relative to H_2SO_4 containing 0.02 mol/litre of Pu^{III}
$\text{Pu}^{\text{V}} \rightarrow \text{Pu}^{\text{IV}}$	Cl_2	0.5 <i>N</i> relative to HCl
	HNO_3	0.5 <i>N</i> relative to HCl
	NH_3OH^+	0.5 <i>N</i> relative to HCl; 0.015 <i>M</i> relative to NH_3OH^+
$\text{Pu}^{\text{VI}} \rightarrow \text{Pu}^{\text{IV}}$	$\text{C}_2\text{O}_4^{2-}$	0.02 <i>M</i> relative to $\text{H}_2\text{C}_2\text{O}_4$
	I^-	2.3 <i>M</i> relative to HI; 3 <i>M</i> relative to HNO_3
	Fe^{2+}	1-2 <i>M</i> relative to HCl

* Pu^{IV} is obtained readily and rapidly electrolytically by oxidizing Pu^{III} on a platinum anode.

or a complex of it (depending on the nature of the anions present). The colour of the Pu^{4+} solutions depends on its ionic state in aqueous solutions.

The conditions of carrying on the oxidation-reduction reactions in the preparation of Pu^{IV} are given in Table 15.1.

Equipment and Reagents

Equipment and Utensils. A spectrophotometer (SF-4, SF-6, SF-8, etc.). Quartz or glass planchets with an absorbing layer 1 cm thick. A water bath. A centrifuge. Glass or quartz test tubes for 15 ml. A calibrated pipette with a syringe.

Radioactive Substances. A 1 *N* solution relative to HNO_3 containing ~ 0.01 mol/litre of Pu^{III} .

Reagents. KBrO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$, Iron(II) sulphamate. Solutions: 1 *N* HCl ; 1 *N* and 12 *M* HNO_3 ; 0.001 *M* KMnO_4 .

Performance of Work

(a) Preparation from Pu^{III} Using Various Oxidizing Agents

Take 10 ml of the initial solution, 1 *N* relative to HNO_3 , containing about 0.01 mol/litre of Pu^{III} (see Sec. A) and divide it into three approximately equal parts in three test tubes. Add a surplus amount with respect to the Pu-containing ion of the oxidizing agent KMnO_4 to the first tube, KBrO_3 to the second, and $\text{K}_2\text{Cr}_2\text{O}_7$ to the third tube, respectively, up to a concentration of ~ 0.1 *M*, with stirring in the cold. Visually watch the change in the colour of the solutions.

Next consecutively transfer the solutions with the aid of the capillary pipette into the quartz or glass planchet and measure the optical density D_{max} against the time *t* at 475-476 nm. Calculate the amount of the oxidized form of Pu^{IV} (in %) in each case using the calibration curve. Arrive at conclusions on the nature of the reaction—slow, fast, or instantaneous—according to the results of measuring D_{max} and the visual observations. For a slow reaction, determine the time needed for oxidation of 50% of the Pu^{III} according to a plot of the amount of the oxidized form of Pu^{IV} (in %) against the time.

*(b) Preparation of Pu^{IV} by the Reaction
of Reducing Pu^{VI} to Pu^{IV}*

Prepare 5-10 ml of the initial 4-6 *M* solution relative to HNO₃ containing ~0.005 mol/litre of Pu^{VI} (see Sec. D, b) in each of two test tubes. Add to one of the solutions with stirring ~0.5 ml of a concentrated solution of hydrazine, and to the other iron(II) sulphamate up to a concentration of 1 *M*. Next transfer the solutions into planchets and measure the optical density D_{max} against the time at 475-476 nm. Calculate the amount of the reduced form of Pu^{IV} (in %) with the aid of the calibration curve.

C. PREPARATION OF Pu^V

Plutonium(V) exists in aqueous solutions in the form of the plutonyl ion PuO₂⁺. Its solutions have a reddish-violet colour. The absorption spectrum of Pu^V has the most intensive bands at wavelengths of 568-569, 770-775, 845, and 1125-1130 nm.

Plutonium(V), as a rule, has a low stability and disproportionates into Pu^{VI} and Pu^{IV} or Pu^{III} in acid solutions. Solutions containing Pu^V at a pH of 4-6 can be retained for a long time, however, because disproportionation in these conditions proceeds quite slowly even at high concentrations of the Pu-containing ion (8-10 g/litre).

**Table 15.2. Conditions of Carrying out Reduction Reactions
Pu^{VI} → Pu^V (at Room Temperature)**

Reducing agent	Composition of solution
16×10 ⁻⁴ <i>N</i> H ₂ SO ₃	5×10 ⁻⁴ mol/litre of Pu ^{VI} ; pH=1.9
0.1 <i>N</i> HNO ₂	17×10 ⁻⁴ mol/litre of Pu ^{IV} ; 0.1 <i>N</i> relative to HNO ₂
I ⁻ *	pH=2
0.05 <i>M</i> H ₂ O ₂	~ 4×10 ⁻⁴ mol/litre of Pu ^{VI} in HClO ₄ ; pH=3.0

* The iodine is removed by extraction with carbon tetrachloride or chloroform.

Plutonium(V) is prepared by reducing Pu^{VI} with various reducing agents or electrolytically.

It is possible to reduce Pu^{VI} only to Pu^{V} in definite conditions (Table 15.2) with the use of mild reducing agents, for example, SO_2 , H_2O_2 , HNO_2 , and I^- .

The most complete electrolytical reduction of Pu^{VI} to Pu^{V} is achieved in perchlorate solutions at 10°C .

When determining the completeness of reduction by the spectrophotometric method, one must dilute the obtained solutions containing Pu^{V} to 0.2 *N* relative to HClO_4 or HNO_3 (to prevent disproportionation). The optical density D_{max} is measured near the wavelengths of 568 or 1130 nm characteristic of Pu^{V} , and 831 nm for Pu^{VI} . The content of Pu^{V} and Pu^{VI} (in %) is determined with the aid of calibration curves or by using the generally known relation $D = \epsilon cd$.

Equipment and Reagents

Equipment and Utensils. A spectrophotometer (SF-4, SF-4A, SF-8, etc.). Quartz or glass planchets (2) with an absorbing layer 1 cm thick. An electronic potentiometer (LP-58, LPU-01, etc.) or a laboratory pH meter ("pH 673"). A quartz beaker for 20-30 ml. Conical flasks for 50-100 ml (4). A capillary pipette; for 2-5 ml. A calibrated pipette with a syringe. Calibrated microburettes for 2-5 ml (2). A stainless steel support.

Radioactive Substances. A 0.05 *N* solution relative to HNO_3 containing ~ 0.01 mol/litre of Pu^{VI} .

Reagents. Solutions: 2 *M* NH_4OH ; ~ 0.1 *N* HClO_4 or NH_4OH ; 0.2 *M* H_2O_2 .

Performance of Work

Reduction with Hydrogen Peroxide

Concentrated solutions containing Pu^{V} and no contaminants are prepared by reducing Pu^{VI} with hydrogen peroxide in nitric acid solutions. The reduction reaction



proceeds with a change in the pH of the solution. Since the lowering of the pH leads to a sharp increase in the rate of disproportionation of the formed Pu^{V} , carry out the reduction with constant monitoring and maintaining of the pH within the selected interval (3-4). This makes it possible to obtain a solution with a Pu^{V} concentration up to ~ 5 g/litre.

Establish a pH of the initial solution equal to 3-4 by adding dropwise a dilute solution of HClO_4 or NH_4OH ($\sim 0.1\text{ N}$).

Arrange the two calibrated microburettes with solutions of H_2O_2 and NH_4OH over the beaker with the obtained solution into which the electrodes of the pH meter are submerged. Add to the initial solution a 0.2 M solution of H_2O_2 dropwise with thorough stirring. Keep the pH of the solution constant by adding when necessary from the second microburette a 2 M solution of NH_4OH . Toward the end of reduction, when a new portion of H_2O_2 is added, the pH changes to a smaller extent, while when reduction is completed, the addition of H_2O_2 is no longer attended by a change in the pH because the 0.2 M solution of H_2O_2 used for this purpose has a pH of about 4.5. The termination of the process of reduction of the Pu^{VI} is also observed according to the appearance of the reddish-violet colour typical of Pu^{V} .

In the process of pH-metric titration, the oxidation state of the plutonium in the solution is also controlled by spectrophotometric means. For this purpose, transfer 3-4 ml of the solution being titrated with the aid of the capillary pipette into a quartz (or glass) planchet and measure its optical density near the wavelengths of 1130-1125, 568, and 831 nm. Use calibration curves or the data contained in Table 15.1 to calculate the amount of reduced and oxidized forms of plutonium (in %), and their ratio depending on the volume of the H_2O_2 added in titration.

The Pu^{V} solutions obtained in this way are stable for a prolonged period. Assume, for example, that the following experimental results were obtained:

Duration of reduction, min	15	30	45	60	75	90
Amount of reduced form of Pu^{V} , % . . .	10	20	45	70	80	95

From these data with the aid of the formula

$$n = n_{\infty} (1 - e^{-kt})$$

(where n and n_{∞} are the amounts of the reduced form of plutonium during the time t and during an infinitely great time, respectively), calculate k —a constant characterizing the process of reducing Pu^{VI} to Pu^{V} .

D. PREPARATION OF Pu^{VI}

Plutonium(VI) exists in acid solutions in the form of the ion PuO_2^{2+} . Its solutions are coloured brown. The spectrum of Pu^{VI} has the most intensive absorption bands in the wavelength regions of 830-833, 953-957, and 983-987 nm. In aqueous solutions, Pu^{VI} is prepared by the oxidation of Pu^{IV} with nitric acid, and also by other oxidizing agents in definite conditions (Table 15.3).

Table 15.3. Conditions of Carrying out Oxidation Reactions
 $\text{Pu}^{\text{IV}} \rightarrow \text{Pu}^{\text{VI}}$ (at Room Temperature)

Oxidizing agent	Composition of solution
BiO_3^-	0.003 mol/litre of Pu^{IV} ; 5 <i>M</i> relative to HNO_3 ; 0.8 g/litre of NaBiO_3
BrO_3^-*	0.2 mol/litre of Pu^{IV} ; 1 <i>N</i> relative to HNO_3 ; 0.1 <i>M</i> relative to KBrO_3
$\text{Cr}_2\text{O}_7^{2-}$	~ 0.008 mol/litre of Pu^{IV} ; 1.5 <i>N</i> relative to HNO_3 ; 5-10 g/litre of $\text{K}_2\text{Cr}_2\text{O}_7$
MnO_4^-	~ 0.005 mol/litre of Pu^{IV} ; 1 <i>N</i> relative to HNO_3 ; 0.01 <i>M</i> relative to KMnO_4
Ce^{4+}	~ 0.005 mol/litre of Pu^{IV} ; 0.5 <i>N</i> relative to HNO_3 ; 0.1 mol/litre of Ce^{IV}
Ag^{2+}	~ 0.005 mol/litre of Pu^{IV} ; 0.01 <i>M</i> relative to Ag^{2+} ; 0.1 <i>M</i> relative to $\text{S}_2\text{O}_8^{2-}$
H_5IO_6	~ 0.005 mol/litre of Pu^{IV} ; 0.22 <i>N</i> relative to HNO_3 ; 0.02 <i>M</i> relative to H_5IO_6

* At a temperature of 80-90 °C.

Equipment and Reagents

Equipment and Utensils. A spectrophotometer (SF-4, SF-8, SF-16, etc.). Glass or quartz planchets (2) with an absorbing layer 1 cm thick. A capillary pipette for 2-3 ml. A calibrated pipette with a syringe. A water bath. Quartz or glass test tubes.

Radioactive Substances. A solution of 1 *N* relative to HNO_3 (or HClO_4) containing ~ 0.01 mol/litre of Pu^{IV} .

Reagents. $\text{K}_2\text{Cr}_2\text{O}_7$. KBrO_3 . KMnO_4 . Solutions: concentrated HNO_3 .

Performance of Work

(a) Oxidation of Pu^{IV} with the Aid of $\text{K}_2\text{Cr}_2\text{O}_7$, KBrO_3 , and KMnO_4

Put 4-5 ml of the initial solution, 1 *N* relative to HNO_3 , containing ~ 0.01 mol/litre of Pu^{IV} with the aid of the pipette into each of three test tubes (glass or quartz). To each test tube add one oxidizing agent: $\text{K}_2\text{Cr}_2\text{O}_7$ (5-10 g/litre), KBrO_3 (0.1 *M*), or KMnO_4 (0.01 *M*). Keep the solution with KMnO_4 at room temperature for one or two hours. Heat the solutions with $\text{K}_2\text{Cr}_2\text{O}_7$ and KBrO_3 on the water bath at 80-90 °C during one hour. Visually observe the change in the colour of all the solutions.

After adding the oxidizing agent, in definite intervals of time (0.5, 1, 1.5, and 2 h) transfer 3-4 ml of the cooled solution into a quartz or glass planchet and measure its optical density at the wavelength of 475-476 nm characteristic of Pu^{IV} , and at 831 nm characteristic of Pu^{VI} . Determine the content of the oxidized form, Pu^{VI} (in %), according to a calibration curve.

On the basis of the results obtained and of visual observation of the change in the solution's colour, determine whether the reaction is slow, fast, or very fast. When the rate of the oxidizing reaction is slow, plot the amount of the oxidized form of Pu^{VI} (in %) against the time elapsed from the instant when the oxidizing agent was added, and determine the duration of oxidizing 50% of the Pu^{IV} .

(b) Oxidation of Pu^{IV} with Nitric Acid

The rate of oxidation of plutonium is greatly affected by the acidity of the solution and by complexing reactions. There is no danger of oxidation when Pu^{IV} is heated in concentrated nitric acid, but it proceeds readily in hot dilute nitric acid.

Prepare 5-10 ml of a 0.2-1.0 *N* solution relative to HNO_3 , containing about 0.005 mol/litre of Pu^{IV} in a quartz beaker or test tube. Heat the solution on a water bath at 90-95 °C during three or four hours, and as the reaction $\text{Pu}^{\text{IV}} \rightarrow \text{Pu}^{\text{VI}}$ proceeds, determine the concentration of Pu^{IV} and Pu^{VI} by the spectrophotometric method in definite time intervals (15 min, 30 min, 1 h, 2 h, etc.). For this purpose, transfer

3-4 ml of the cooled solution by means of the capillary pipette into a glass or quartz planchet and measure its optical density at wavelengths of 475-476 and 831 nm. Next use the calibration curves to find the degree of oxidation of Pu^{IV} to Pu^{VI} at the chosen acidity of the solution and the given plutonium concentration. If the reaction is slow, also determine the time needed for oxidizing the Pu^{IV} by 50% (see Sec. a). Combine the working solution with the initial one that is used in subsequent experiments.

E. PREPARATION OF Pu^{VII}

Work with Pu^{VII} requires increased attention to the purity of the working solutions and reagents. Not all the reagents used in the oxidation of Np^{VI} are suitable for preparing Pu^{VII} (see p. 184).

The reactions of preparing Pu^{VII} with the use, for example, of oxidizing agents such as hypobromite, hypochlorite, permanganate, and ferricyanide ions, silver oxide, and Am^{VI} proceed sufficiently completely only in strong alkalis ($>7-10\text{ M}$). As with Np^{VII} , to prepare Pu^{VII} , the methods of ozonization and electrolytic anode oxidation of plutonium (on platinum, lead dioxide, and nickel) are used, which are the most important from a practical standpoint. Dilute solutions of alkalis containing Pu^{VI} are greenish-blue, while more concentrated solutions are black.

Equipment and Reagents

Equipment and Utensils. A spectrophotometer (SF-4, SF-6, etc.). An ozonizer. Glass or quartz planchets with an absorbing layer 1 cm thick (3). A water bath. Glass test tubes for 10-15 ml (5). A capillary pipette for 2-3 ml.

Radioactive Substances. A suspension of sodium plutonate. A solution ($\sim 10\text{ ml}$) containing $\sim 1 \times 10^{-3}\text{ mol/litre}$ of Pu^{VI} (the mother liquor after separating the plutonate or hydroxide precipitate).

Reagents. Ozone. $\text{K}_2\text{S}_2\text{O}_8$. KBrO . $\text{K}_3\text{Fe}(\text{CN})_6$. Silver oxide. Solutions: concentrated NaOH , KOH .

Performance of Work

(a) Add 4-5 ml of a 3 *N* solution of NaOH to a test tube containing a suspension of sodium plutonate ($\text{Na}_2\text{PuO}_4 \cdot n\text{H}_2\text{O}$) or 4-5 ml of a weakly alkaline solution ($\text{pH} \approx 8.5$)

containing about 0.01 mol/litre of Pu^{VI} . Ozonize the solution (at a rate of passing the gas mixture of ~ 8 litre/h through 5 ml of the solution). Perform the work at room temperature during 20-30 min.

(b) To 4-5 ml of a 0.8-0.9 *N* solution relative to KOH containing about 1×10^{-3} mol/litre of Pu^{VI} (the mother liquor after separating the plutonate or hydroxide precipitate) in a test tube, add $\text{K}_2\text{S}_2\text{O}_8$ up to a concentration of 0.1-0.2 *M* and heat the solution during about 20 min at 80-90 °C.

(c) Prepare 4-5 ml of the initial solution containing about 1×10^{-3} mol/litre of Pu^{VI} (as indicated in Sec. b) in a test tube. Prepare Pu^{VII} in one of the following ways.

(1) Add KOH to the initial solution up to a concentration of ~ 12 *M* and KBrO to a 0.1 *M* with following heating at 70-90 °C during 15-20 min.

(2) Add KOH to the initial solution up to a concentration of ~ 12 *M* and $\text{K}_3\text{Fe}(\text{CN})_6$ up to $\sim 5 \times 10^{-3}$ *M* in the cold.

(3) Add NaOH to the initial solution up to a concentration of 10 *M* and 2-5 mg/ml of silver oxide with following heating at 80-90 °C during about 15 min.

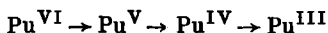
(4) Add NaOH to the initial solution up to a concentration of 10-14 *M* and KMnO_4 to ~ 0.1 *M* in the cold.

Determine the fraction of oxidized Pu^{VI} by measuring the optical density of the solution at 635 nm. According to the results of measuring D_{max} and visual observation of the change in the colour of the solutions, arrive at conclusions on the nature of the reaction: slow, fast, or instantaneous. If the reaction is slow, determine the time needed for oxidizing half of the Pu^{VI} .

Experiment 15.2. KINETICS OF PLUTONIUM OXIDATION-REDUCTION REACTIONS [2, 4]

The investigation of the oxidation-reduction properties of actinides, including plutonium, requires a knowledge of the rates of the reactions. As an example of studying the kinetics of the reactions, we can indicate the problem of determining the rate constants of the transition of Pu^{VI} to the lower oxidation states.

The reduction of Pu^{VI} to Pu^{III} by hydrazine proceeds in three consecutive steps:



whose rates are commensurable; the reduction of Pu^{V} occurs both at the expense of the direct interaction with the hydrazine and at the expense of disproportionation, more exactly at the expense of the reaction of PuO_2^+ and Pu^{3+} ions. A spectrophotometer can be employed to observe the using up of the Pu^{VI} in time, the consecutive formation of Pu^{V} and Pu^{IV} and their using up, and, finally, the formation of the reaction product— Pu^{III} . It is also possible to determine the rate constant of the first step of the reaction, i.e. the transition of Pu^{VI} to Pu^{V} , which according to published data [5] observes the kinetic equation

$$-\frac{d[\text{Pu}^{\text{VI}}]}{dt} = k \frac{[\text{Pu}^{\text{VI}}][\text{N}_2\text{H}_4]}{[\text{H}^+]}$$

where $k = 0.314 \text{ min}^{-1}$ at 40°C and $k = 3.0 \text{ min}^{-1}$ at 70°C and an ionic strength of $\mu = 2$.

Equipment and Reagents

Equipment and Utensils. A spectrophotometer (SF-4, SF-4A, SF-8, etc.) provided with a thermostatted planchet holder. Glass or quartz planchets (2) with an absorbing layer 1 or 2 cm thick. A capillary pipette for 2-3 ml. A calibrated pipette with a syringe. A water bath. Glass or quartz test tubes.

Radioactive Substances. A 1 *N* solution relative to HNO_3 containing about 0.04 mol/litre of Pu^{VI} .

Solutions: $\sim 5 \text{ M}$ NaNO_3 and $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$; concentrated HNO_3 .

Performance of Work

Pour solutions of $\text{PuO}_2(\text{NO}_3)_2$, HNO_3 , NaNO_3 , and water into the working planchet to obtain concentrations of them of $2 \times 10^{-3} \text{ M}$, 1 *M*, and 1 *M*, respectively; stir the solution and keep it until a temperature of 70°C is reached. Next add a solution of hydrazine up to its concentration of 0.1 *M* and register the change in the optical density in time in the region of the peaks at 830, 475, and 600 nm. Upon completion of the reaction, i.e. after a growth in *D* stops at 600 nm, calculate the concentrations of Pu^{VI} , Pu^{IV} , and Pu^{III} from the values of the density at these wavelengths, introducing corrections for the absorption of plutonium in other oxidation states. Calculate the concentration of Pu^{V} for each instant according to the difference between the total concentration of Pu and the sum of the concentrations

of its other forms. Plot kinetic curves of the change in the concentrations of all the oxidation states of plutonium.

To determine the rate constant of the reaction of the transition of Pu^{VI} to Pu^{V} , plot $\log [\text{Pu}^{\text{VI}}]$ against the time and calculate the first-order rate constant from the slope of the straight line: $k' = 2.3 \tan \alpha$.

Next determine the total rate constant of the reaction (in s^{-1}) by the formula

$$k = k' \frac{[\text{H}^+]}{[\text{N}_2\text{H}_4]}$$

and compare it with the value found in [2].

Experiment 15.3. DETERMINATION OF OXIDATION-REDUCTION POTENTIALS OF Pu IONS [4, 6-8]

Only the oxidation-reduction potentials of the pairs $\text{Pu}^{\text{III}}\text{-Pu}^{\text{IV}}$ and $\text{Pu}^{\text{V}}\text{-Pu}^{\text{VI}}$ lend themselves to direct measurement. The values of the potentials of other ion pairs of plutonium obtained with breaking or formation of a metal-oxygen bond are determined by calculation.

To measure the oxidation-reduction potentials of plutonium, the solution being investigated is placed in a conventional electrolytic cell having four outlets. Two of them are used for the connecting bridges, the third for the passage of gas and taking samples, and the fourth for the platinized platinum electrode customarily used when working with plutonium. The solution is stirred by rotation of the electrode made in the form of a platinum wire loop. The current from the electrode is brought out along an insulated conductor laid in an opening drilled in the centre of the load-carrying axle, and is removed by a copper-graphite plate from a rotating copper ring secured on an ebonite sleeve mounted on the same load-carrying axle. During the measurements, the temperature of the solution is kept constant within the limits of $20 \pm 0.1^\circ \text{C}$ by the water fed into the jacket of the cell from a thermostat. The cell is ground in to the device for rotating the electrode, which makes it possible to measure the oxidation-reduction potentials in an atmosphere of an inert gas, for example, nitrogen. The nitrogen is preliminarily purified of oxygen by passing it through an installation consisting of three

consecutively connected tubes filled respectively with CaCl_2 , activated carbon, and copper dispersed on silica gel and heated to 250°C .

Equipment and Reagents

Equipment and Utensils. A spectrophotometer (SF-4, SF-4A, SF-8, etc.). Glass or quartz planchets (2) with an absorbing layer 1 cm thick. A cell for measuring the potential (20-30 ml). An installation for purifying nitrogen. A thermostat. An electron potentiometer (LP-58, LPU-01, etc.) or a laboratory pH meter ("pH 673"). A test tube for 10-15 ml. A capillary pipette for 2-5 ml. A microburette for 2-5 ml. A quartz beaker for 40-50 ml.

Radioactive Substances. A solution (15-20 ml), 0.2-0.4 N relative to HNO_3 , containing 0.01 mol/litre of Pu^{IV} .

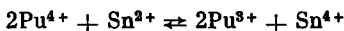
Reagents. Solutions: 0.2-0.4 N and 3-4 M HNO_3 ; 4 M and concentrated HClO_4 ; 3-4 M NaOH ; 3-4 M HCl ; 0.1 M NaI ; 30% H_2O_2 ; mixed—0.1 M relative to SnCl_2 and 1 N relative to HClO_4 ; mixed—0.1 M relative to SnCl_2 and 1 N relative to HCl .

Performance of Work

(a) Determination of E_f for $\text{Pu}^{\text{III}}\text{-Pu}^{\text{IV}}$ in a 1 N Solution of HClO_4

Prepare 10 ml of a 1 N solution relative to HClO_4 containing 0.01 mol/litre of Pu^{IV} in the quartz beaker. For this purpose, precipitate the plutonium from a nitric acid solution in the form of the hydroxide, and after dissolving it in a 4 M solution of HClO_4 establish the given composition of the initial solution. Next transfer the solution into the electrolytic cell, which is thermostatted (25°C).

To prepare Pu^{III} by reducing Pu^{IV} , use the 2-5-ml microburette to add a mixed solution of 0.1 M relative to SnCl_2 and 1 N relative to HClO_4 in small portions to the initial solution (with thorough mixing during 1-2 min). After each addition, measure the potential of the system relative to a standard calomel electrode. For all the values of E_{meas} , determine the ratio $[\text{Pu}^{4+}]/[\text{Pu}^{3+}]$ according to the amount of added SnCl_2 proceeding from the reaction



Calculate the mean value of the formal potential E_f (in mV) for the pair $\text{Pu}^{\text{III}}\text{-Pu}^{\text{IV}}$ in a 1 N solution of HClO_4

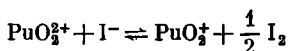
by the formula

$$E_{\text{meas}} = E_f + 250 + 59 \log \frac{[\text{Pu}^{\text{IV}}]}{[\text{Pu}^{\text{III}}]}$$

In a similar way, determine E_f for $\text{Pu}^{\text{III}}\text{-Pu}^{\text{IV}}$ in a 1 *N* solution of HCl .

*(b) Determination of E_f for $\text{Pu}^{\text{V}}\text{-Pu}^{\text{VI}}$
in a 0.1 *N* Solution of HClO_4*

Prepare 10 ml of the initial 0.1 *N* solution relative to HClO_4 (or HCl) containing 0.01 mol/litre of Pu^{VI} in the quartz beaker. Next establish a pH of 3 with the aid of the electronic potentiometer or pH meter (add dropwise a 3 *M* solution of NaOH), and transfer the solution into the electrolytic cell. According to the procedure described above (see Sec. a) perform potentiometric titration of the initial solution, adding small portions of a 0.1 *M* solution of NaI with thorough stirring during two or three minutes. For the found values of E_{meas} , determine the ratio $[\text{Pu}^{\text{VI}}]/[\text{Pu}^{\text{V}}]$ according to the amount of added NaI proceeding from the reaction



Calculate the mean value of the formal potential for the pair $\text{Pu}^{\text{V}}\text{-Pu}^{\text{VI}}$ in 0.1 *N* HClO_4 (or HCl) by the formula given in Sec. a.

In a similar way determine the potential for the pair $\text{Pu}^{\text{VI}}\text{-Pu}^{\text{V}}$ at a pH of 3 or 4, obtaining Pu^{V} by reducing Pu^{VI} with the action of another reducing agent suitable for this purpose, for example H_2O_2 (see Experiment 15.1C) or electrolytically (in the cathode space of the cell at a potential on the cathode of 0.90 V).

When performing this experiment, give attention to the purity of the initial solution relative to the lower oxidation states of plutonium.

**Experiment 15.4. EQUILIBRIUM BETWEEN
DIFFERENT OXIDATION STATES OF Pu
IN AQUEOUS SOLUTIONS [4, 6-8]**

Plutonium ions of all oxidation states in appreciable concentrations can exist in equilibrium in acid solutions. Some of them experience disproportionation reactions,

which is due to the closeness of the potentials of transition of plutonium from one oxidation state to another and the features of the structure of its electron shell: the presence of free 5*f*-orbitals makes possible the transfer of electrons from one plutonium ion to another according to the donor-acceptor mechanism.

Equipment and Reagents

Equipment and Utensils. A spectrophotometer (SF-4, SF-6, etc.). Quartz or glass planchets (2) with an absorbing layer 1 cm thick. A water bath. A centrifuge. A thermostat. Quartz or glass test tubes for 20 ml (4). A capillary pipette for 2-5 ml. A calibrated pipette with a syringe. Conical flasks for 50-100 ml (3). Stainless steel supports.

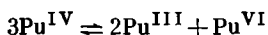
Radioactive Substances. A 1 *N* solution (~ 10 ml) relative to HNO_3 containing 0.02 mol/litre of Pu^{IV} .

Reagents. Solutions: 0.1 *N* and concentrated NH_4OH ; 1-2 *N* KOH ; 0.1 *N* and concentrated HCl ; 1 *N* HNO_3 .

Performance of Work

(a) Disproportionation of Pu^{IV} in Solutions of HCl and HNO_3

The disproportionation of Pu^{IV} in solutions of HCl of a moderate concentration (~ 2.0 - 0.2 *N*) proceeds according to the equation



At a concentration of the HCl under 0.2 *N*, Pu^{V} accumulates in addition to Pu^{III} and Pu^{VI} .

After heating 5 ml of the initial solution of 1 *N* relative to HNO_3 containing ~ 0.02 mol/litre of Pu^{IV} in a test tube on a water bath to $\sim 90^\circ\text{C}$, add a concentrated solution of NH_4OH or 1-2 *N* KOH in portions while stirring with a glass rod up to an alkaline reaction ($\text{pH} > 10$). Separate the precipitate of $\text{Pu}(\text{OH})_4 \cdot n\text{H}_2\text{O}$ by centrifuging and after decanting the mother liquor wash it 2-3 times with a 0.1 *N* solution relative to HCl (3-4 ml). Next dissolve the precipitate in a minimum volume (2-3 ml) of concentrat-

* When performing work involving the disproportionation of Pu^{IV} and Pu^{V} in nitric acid solutions, to avoid auxiliary processes introducing complications, use nitric acid free of nitrous acid and nitrogen oxides.

ed hydrochloric acid with heating on the water bath (70 °C) during several minutes. Use this solution to prepare working solutions of various concentrations by diluting its aliquot part (~0.5 ml) with hydrochloric acid:

(1) 0.2 *N* relative to HCl containing 0.004 mol/litre of Pu^{IV};

(2) 0.5 *N* relative to HCl containing 0.004 mol/litre of Pu^{IV};

(3) 0.2 *N* relative to HCl containing 0.001 mol/litre of Pu^{IV}.

Use spectrophotometric techniques to determine the changes in the concentration of plutonium in various oxidation states at room temperature depending on the time elapsed from the instant of preparing the relevant working solution: 0.5, 1, 2, 5 h and at equilibrium (1-2 days). Simultaneously measure the optical density *D* at wavelengths of 470, 603, and 831 nm. Evaluate the concentration of the plutonium in the relevant oxidation state *c*_{III}, *c*_{IV}, and *c*_{VI} by solving the simultaneous equations

$$D_{470} = \varepsilon'_{III}c_{III} + \varepsilon'_{IV}c_{IV} + \varepsilon'_{VI}c_{VI}$$

$$D_{603} = \varepsilon''_{III}c_{III} + \varepsilon''_{IV}c_{IV} + \varepsilon''_{VI}c_{VI}$$

$$D_{831} = \varepsilon'''_{III}c_{III} + \varepsilon'''_{IV}c_{IV} + \varepsilon'''_{VI}c_{VI} \quad (\text{at } d = 1 \text{ cm})$$

where ε'_{III} , ε'_{IV} , and ε'_{VI} are the molar absorption coefficients of Pu^{III}, Pu^{IV}, and Pu^{VI} at $\lambda = 470$ nm; ε''_{III} , ε''_{IV} , and ε''_{VI} are the same at $\lambda = 603$ nm, and ε'''_{III} , ε'''_{IV} , and ε'''_{VI} are the same at $\lambda = 831$ nm.

Also calculate the concentration equilibrium constant:

$$K = \frac{[\text{Pu}^{III}]^3 [\text{Pu}^{VI}]}{[\text{Pu}^{IV}]^3}$$

Enter the results of the calculations in a table as shown below:

Time from beginning of experiment, h	Pu ^{III} , %	Pu ^{IV} , %	Pu ^{VI} , %	<i>K</i>	$\sum [\text{Pu}]_{\text{calc}}, \%$

Determine the duration of disproportionation of Pu^{IV} by 50% ($t_{1/2}$) relative to the equilibrium value.

Qualitatively, by comparing the obtained disproportionation times $t_{1/2}$, determine the influence of the concentration of H^+ ions and Pu^{IV} in the initial solution on the rate and depth of proceeding of the Pu^{IV} disproportionation reaction.

(b) Disproportionation of Pu^{V} in Solutions of HCl and HNO_3

In a 0.5 N solution relative to HCl , the disproportionation of Pu^{V} proceeds relatively slowly, which makes it possible to determine the rate of this reaction.

Prepare ~ 10 ml of a nitric acid solution with a pH of 3 or 4 containing 0.004 mol/litre of Pu^{V} (see Experiment 15.1C). Bring the acidity of the solution up to 0.5 N relative to HCl and rapidly determine the concentration in the initial solution obtained. Next, also rapidly, transfer a portion of it (3-4 ml) with the aid of the capillary pipette into a quartz or glass planchet for spectrophotometric measurements. Measure the optical density of the solution in definite time intervals (0.5, 1, 2, 4 h, etc.) until equilibrium is reached between the different oxidation states of plutonium at wavelengths of 603, 470, 568-569, and 831 nm, corresponding to the absorption peaks for Pu^{III} , Pu^{IV} , Pu^{V} , and Pu^{VI} , respectively. In the intervals between the measurements, keep the solution in the thermostat at $25 \pm 0.1^\circ\text{C}$.

Use the experimental results to calculate the concentrations of the separate forms of plutonium (in %) for a different time elapsed from the instant of the beginning of measurements (in hours). On the basis of the found values of the concentrations of the various plutonium ions, determine the values of the concentration equilibrium constants:

$$K_1 = \frac{[\text{Pu}^{\text{VI}}] [\text{Pu}^{\text{III}}]}{[\text{Pu}^{\text{IV}}] [\text{Pu}^{\text{V}}]} \quad \text{and} \quad K_2 = \frac{[\text{Pu}^{\text{III}}]^2 [\text{Pu}^{\text{VI}}]}{[\text{Pu}^{\text{IV}}]^3}$$

and the time of disproportionation of Pu^{V} by 50% (see Sec. a).

Perform similar work with a 0.3 N solution relative to HNO_3 containing 0.007 mol/litre of Pu^{V} and compare the results obtained with the preceding ones.

Experiment 15.5. DISTRIBUTION OF Pu BETWEEN SOLUTION AND SOLID PHASE [9]

Plutonium coprecipitation processes are the basis of methods first used for its separation. In its lower oxidation states, plutonium coprecipitates well with fluorides, sulphates, phosphates, oxalates, and a number of other organic coprecipitants. A specific carrier for Pu^{VI} is sodium uranyl-triacetate.

Perform the work in a class III laboratory in sealed fume cupboards.

Equipment and Reagents

Equipment and Utensils. A counting installation with a scintillation detector of α -radiation and an end-window β -counter. A device for determining solubility. A centrifuge. A thermostat. A water bath. A liquid proportioner. Quartz or glass test tubes for 10-15 ml (4). Conical flasks for 50-100 ml (3). Measuring cylinders for 100 ml (5). A calibrated pipette with a syringe.

Radioactive Substances. A 1 *N* solution relative to HNO_3 (5-6 ml) containing 5×10^{-4} mol/litre of Pu^{IV} (see Experiment 15.1). A 1 *N* solution relative to HNO_3 (30-40 ml) containing ^{239}Np with a specific activity of $\sim 10^4$ cpm/ml and ^{239}Pu with a specific activity of 4×10^5 cpm/ml.

Reagents. $\text{La}(\text{NO}_3)_3$. K_2SO_4 . $\text{K}_3\text{La}(\text{SO}_4)_3$. SO_2 (in a cylinder). $\text{K}_2\text{Cr}_2\text{O}_7$. $\text{Zr}(\text{C}_6\text{H}_5\text{AsO}_3)_2$.

Performance of Work

Coprecipitation of Pu^{III} and Pu^{IV} with $\text{K}_3\text{La}(\text{SO}_4)_3$

In definite conditions, Pu^{III} and Pu^{IV} are coprecipitated from aqueous solutions with a precipitate of $\text{K}_3\text{La}(\text{SO}_4)_3$, which forms the basis of the sulphate method of separating plutonium.

In a 100-ml measuring cylinder, prepare 30-40 ml of a solution containing ^{239}Pu (with a specific activity of $\sim 4 \times 10^5$ cpm/ml), 5-7% with respect to HNO_3 , 1% with respect to SO_2 , and containing 0.2-0.3 mg/ml of La.

Introduce the plutonium-239 by adding 1 ml of the initial solution of 1 *N* relative to HNO_3 containing 5×10^{-4} mol/litre of Pu^{IV} . Saturate the solution with SO_2 while heating on the water bath up to 90-95 °C during 30 min for obtaining plutonium in the +3 oxidation state.

In a second measuring cylinder, also prepare 30-40 ml of a solution containing ^{239}Pu (with a specific activity of $\sim 4 \times 10^5$ cpm/ml) 5-7% with respect to HNO_3 , and add to the solution 0.15 g of $\text{K}_3\text{La}(\text{SO}_4)_3$ and 0.19 mol of K_2SO_4 .

Prepare the double salt $\text{K}_3\text{La}(\text{SO}_4)_3$ beforehand and introduce it into the solution according to the calculations; introduce the ^{239}Pu by adding 1 ml of a 1 *N* solution relative to HNO_3 containing about 5×10^{-4} mol/litre of Pu^{IV} .

Saturate the solution in the first cylinder with K_2SO_4 up to 0.7 *M*, let the precipitate settle during 30 min, after which bring the concentration of the K_2SO_4 up to 1.1 *M* and again let the precipitate settle during 30 min. The total duration of precipitation is one hour.

Separate the phases by decanting or by removing the solution using the pipette with the syringe. Dilute an aliquot part of the solution with nitric acid (0.5-1.0 *N*) from 50 to 100 times, take (with the aid of the liquid proportioner) two or three parallel samples each containing 0.09 ml of the solution, and measure the α -activity of the solution before and after precipitating the $\text{K}_3\text{La}(\text{SO}_4)_3$. Calculate the amount of coprecipitated Pu^{III} (in %).

In the second cylinder, coprecipitate Pu^{IV} with $\text{K}_3\text{La}(\text{SO}_4)_3$ by the method of crystallizing the solid phase from the obtained supersaturated solution with rapid mechanical stirring and at a constant temperature of $25 \pm 0.1^\circ\text{C}$ (in the thermostat). Monitor the degree of oxidation of the plutonium by coprecipitating Pu^{IV} with a precipitate of zirconium phenylarsonate $\text{Zr}(\text{C}_6\text{H}_5\text{AsO}_3)_2$. After eliminating the supersaturation in the solution, measure the α -activity of the liquid phase. Use the well known Doerner-Hoskins (logarithmic) distribution law to evaluate the constant λ .

Experiment 15.6. DISTRIBUTION OF Pu BETWEEN WATER AND AN ORGANIC SOLVENT [10-12]

The extraction of plutonium from aqueous solutions with organic solvents is employed for separating small amounts of it from an enormous mass of uranium fuel. Plutonium is usually extracted with solvents in nitrate systems because complexing ligands such as SO_4^{2-} , PO_4^{3-} , and $\text{C}_2\text{O}_4^{2-}$ lower the distribution coefficients. The most important and frequently used extractants for plutonium include tributyl

phosphate (TBP), methylisobutyl ketone (hexone), diethyl ether, amines, tenoyl trifluoroacetone (TTA), cupferron, and dibutylcarbitol.

Equipment and Reagents

Equipment and Utensils. A counter with a scintillation detector of α -radiation. A water bath. A shaker or a vibrator controlled with the aid of an autotransformer. A liquid proportioner. A separatory funnel for 150-200 ml. Test tubes for 10-15 ml (10). Conical flasks for 100-200 ml (4). A capillary pipette for 2-5 ml. A calibrated pipette with a syringe. Chemical beakers for 100 ml. A stainless steel support. Measuring cylinders for 50 ml (5).

Radioactive Substances. A 1 *N* solution relative to HNO_3 (10 ml) containing ~ 0.005 mol/litre of Pu^{IV} .

Reagents. (a) Charcoal. NaNO_3 . $\text{Ca}(\text{NO}_3)_2$. $\text{Al}(\text{NO}_3)_3$. NH_4NO_3 . $(\text{NH}_4\text{SO}_3\text{O})_3\text{Fe}$. $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$ (or rongalite). Solutions: 0.1, 1, and 2 *N* and 7 *M* HNO_3 ; 5% Na_2CO_3 (or 2% NaOH); 20% TBP in purified kerosene, synthine, benzene, or CCl_4 .

(b) *N*-benzoylphenylhydroxylamine. Solutions: 3 *M* HNO_3 ; 1 *N* and 3 *M* H_2SO_4 ; 0.5 and 3 *M* $(\text{NH}_4)_2\text{SO}_4$; 0.6 *M* $\text{H}_2\text{C}_2\text{O}_4$. 1% ethyl alcohol.

Performance of Work

(a) Extraction of Pu^{IV} and Pu^{VI} with Tributylphosphate

TBP extracts Pu^{IV} and Pu^{VI} quite well, whereas Pu^{III} is virtually not extracted. As a result, conditions are created for running extraction cycles with the aim of extracting plutonium from irradiated uranium.

For extraction, use solutions of TBP in an inert diluent, for example in purified kerosene, synthine, benzene, or carbon tetrachloride. To purify the TBP, preliminarily treat it with an equal volume of 5% solution of Na_2CO_3 (or 1-2% NaOH), then wash it several times with dilute HNO_3 and distilled water up to a neutral reaction, bring it into contact with charcoal, and filter it off.

Put two portions (3-5 ml) of an initial solution of 1 *N* relative to HNO_3 containing 0.005 mol/litre of Pu^{IV} into 10-ml test tubes with the aid of the capillary pipette. To prepare Pu^{III} , add formaldehyde sodium sulphonylate (5-10 g/litre) to one of the solutions. Pu^{VI} is prepared by oxidizing Pu^{IV} by 0.5-1.0 *N* nitric acid while heating in a test tube on the water bath at 80-90 °C during one or two

hours. Monitor the degree of oxidation of the plutonium by the spectrophotometric method.

Prepare three solutions (15-20 ml each) of 2 *N* relative to HNO_3 containing ^{239}Pu with a specific activity of $\sim 4 \times 10^5$ cpm/ml in the oxidation states +3, +4, and +6 simultaneously in measuring cylinders. For this purpose, to each of the 2 *N* solutions relative to HNO_3 add 0.1 ml of a solution containing ~ 0.005 mol/litre of plutonium in the relevant oxidation state. Take two or three samples of each of these solutions for measuring the α -activity, using the liquid proportioner.

Transfer the solutions consecutively into the separatory funnel and extract the Pu^{III} , Pu^{IV} , and Pu^{VI} with an equal volume of a 20% solution of TBP, vigorously shaking it during five minutes at room temperature. After settling and separation of the phases, measure the α -activity in them. Calculate the values of K_d , and also the extraction of Pu^{III} , Pu^{IV} , and Pu^{VI} into the organic phase (in %).

(b) Extraction of Pu^{IV} with the Aid of N-Benzoylphenylhydroxylamine

Pu^{IV} can be extracted in the form of an intracomplex compound with the aid of N-benzoylphenylhydroxylamine (BPHA). For this purpose, purify the BPHA by threefold recrystallization from hot water. Use as the solvent chloroform washed consecutively with a dilute solution of NaOH and water, then dried with sodium sulphate and distilled. Add 1% ethanol to it for stabilization after distilling it.

Prepare (30-40 ml each) the following solutions containing $^{239}\text{Pu}^{\text{IV}}$ (with a specific activity of $\sim 4 \times 10^5$ cpm/ml):

- (1) 3 *M* relative to HNO_3 ;
- (2) 0.5 *M* relative to H_2SO_4 ;
- (3) 3 *M* relative to H_2SO_4 ;
- (4) 0.5 *M* relative to $(\text{NH}_4)_2\text{SO}_4$;
- (5) 3 *M* relative to $(\text{NH}_4)_2\text{SO}_4$;
- (6) 0.6 *M* relative to $\text{H}_2\text{C}_2\text{O}_4$ (see Sec. a).

Consecutively transfer the solutions into the separatory funnel and perform extraction with an equal volume of a 0.3-0.4 *M* solution of BPHA while shaking for 0.5-1 min at room temperature. After settling and separation of the aqueous and organic phases, take two or three samples

(0.09 ml each) from each solution for measuring the α -activity. Calculate the distribution coefficients of Pu^{IV} and its extraction (in %) into the organic phase. Arrive at the relevant conclusions on how various factors (the nature and concentration of the acid, complexing agent, etc.) affect the extraction of the complex of Pu^{IV} with BPHA by means of chloroform.

Experiment 15.7. COMPLEXING OF Pu IN AQUEOUS SOLUTIONS [13-15]

The methods of solubility, ion exchange, extraction, spectrophotometry, and potentiometry are widely used to study the complexing of actinides, including plutonium, in aqueous solutions.

A. DETERMINING THE SOLUBILITY PRODUCT AND THE STABILITY CONSTANT OF AN OXALATE COMPLEX

The solubility product P_s of various compounds is usually determined by studying the solubility of precipitates in acids with the use of equations first proposed by A. Babko and K. Yatsimirsky. This method is especially convenient when there is no possibility of directly determining P_s of a compound according to data on its solubility in water. The same experimental data are used, with the aid of a relevant relations, to find also the composition and stability constants of the complexes of a metal-containing ion formed in a system.

To determine, for example, $P_s(\text{PuO}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O})$ and β_j of the oxalate complexes of Pu^{VI} , experimental data are obtained on the solubility of $\text{PuO}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ in mixed solutions of HNO_3 and $\text{H}_2\text{C}_2\text{O}_4$ of a varying composition.

Equipment and Reagents

Equipment and Utensils. A counter with a scintillation detector of α -radiation. A device for determining solubility with a water-salt seal. A thermostat. A liquid proportioner. Quartz or glass test tubes for 10 ml (3-4). Conical and measuring flasks for 50-100 ml (4). A capillary pipette for 2-5 ml. A calibrated pipette with a syringe. Chemical beakers for 100 ml. Stainless steel supports.

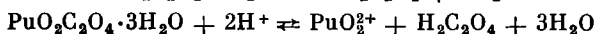
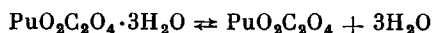
Radioactive Substances. A 1 *N* solution (~ 15 -20 ml) relative to HNO_3 containing 0.01 mol/litre of Pu^{VI} .

Reagents. Oxalic acid. A concentrated solution of HNO_3 .

Performance of Work

Prepare a precipitate of plutonyl oxalate (see Experiment 15.8b). Use a conventional procedure to determine its solubility in mixed solutions of HNO_3 and $\text{H}_2\text{C}_2\text{O}_4$ at a concentration of the HNO_3 equal to 2 *N* and at concentrations of the $\text{H}_2\text{C}_2\text{O}_4$ varying from 0.1 to 0.4 *M*.

Determine $P_s(\text{PuO}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O})$ and the concentration constant of stability of the complex $[\text{PuO}_2\text{C}_2\text{O}_4]^0$ (at $\mu = 2$) proceeding from the fact that the processes of dissolving of plutonyl oxalate are expressed by the equations



whence

$$L = [\text{PuO}_2\text{C}_2\text{O}_4] + [\text{PuO}_2^{2+}]$$

or

$$L = K_1 + \frac{K_2 [\text{H}^+]^2}{[\text{H}_2\text{C}_2\text{O}_4]}$$

where K_1 and K_2 are the concentration equilibrium constants of the reactions.

Using the value of $K_1 = 2.2 \times 10^{-3}$, we obtain

$$K_2 = \frac{[L - 2.2 \times 10^{-3}] [\text{H}_2\text{C}_2\text{O}_4]}{[\text{H}^+]^2}$$

where $[\text{H}_2\text{C}_2\text{O}_4] \approx \Sigma[\text{H}_2\text{C}_2\text{O}_4]$ is the initial concentration of the oxalic acid; $[\text{H}^+] = 2$ *N*.

The mean value of the constant K_2 found in this way is used to calculate $P_s(\text{PuO}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O})$ by the equation

$$K_2 = \frac{[\text{PuO}_2^{2+}] [\text{H}_2\text{C}_2\text{O}_4] [\text{C}_2\text{O}_4^{2-}]}{[\text{H}^+]^2 [\text{C}_2\text{O}_4^{2-}]} = \frac{P_s}{K' K''}$$

where K' and K'' are the stepwise dissociation constants of $\text{H}_2\text{C}_2\text{O}_4$. Consequently,

$$P_s(\text{PuO}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}) = K_2 K' K''$$

The stability constant β_1 is calculated by the equation

$$\beta_1 = \frac{[\text{PuO}_2\text{C}_2\text{O}_4]}{[\text{PuO}_2^{2+}] [\text{C}_2\text{O}_4^{2-}]} = \frac{K_1}{P_s(\text{PuO}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O})}$$

The quantity $P_s(\text{PuO}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O})$ is determined graphically from the equation

$$L = [\text{PuO}_2^{2+}] + \beta_1[\text{PuO}_2^{2+}][\text{C}_2\text{O}_4^{2-}]$$

or

$$y = L[\text{C}_2\text{O}_4^{2-}] = P_s + \beta_1[\text{C}_2\text{O}_4^{2-}]P_s$$

At $[\text{C}_2\text{O}_4^{2-}] \rightarrow 0$, the function y tends to its limiting value, namely, $P_s(\text{PuO}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O})$. When $\log y$ is plotted against the concentration of the ligand $\text{C}_2\text{O}_4^{2-}$ in semilogarithmic coordinates and the curve is extrapolated to the axis of ordinates, the ordinate intercept equals $\log P_s$.

B. DETERMINING THE COMPOSITION AND THE STABILITY CONSTANTS OF Pu^{III} COMPLEXES BY THE ION-EXCHANGE METHOD

In the ion-exchange investigation of complexing processes, what is studied is the distribution of indicator amounts of ^{239}Pu between the solution and the adsorbent at a constant value of the pH and a varying concentration of the complexing agent, or vice versa. (When tracer amounts of plutonium are used, there is no need of taking into account the concentration of the addend bound in the complex.) To maintain a constant ionic strength μ , NH_4Cl is added to the solutions. The various oxidation states of plutonium are stabilized as indicated in Experiment 15.1.

Equipment and Reagents

Equipment and Utensils. A counter with a scintillation detector of α -radiation. An electronic potentiometer (LP-58, LPU-01, etc.) or a laboratory pH meter ("pH 673"). A shaker. A liquid proportioner. Glass test tubes or flasks (15) with ground-glass stoppers for 50 ml. A capillary pipette for 2-3 ml. A burette for 25 ml. Chemical beakers for 50-100 ml. Stainless steel supports.

Radioactive Substances. A 1 *N* solution relative to HNO_3 (10-15 ml) containing ~ 0.005 mol/litre of Pu^{IV} .

Reagents. NH_4Cl . Acids: concentrated acetic, 0.5 *M* lactic; 0.0001 *M* nitrilotriacetic. Cation exchanger KU-2 in the NH_4^+ form (grain size 50-70 mesh). Solutions: 1 *N* HNO_3 ; dilute (~ 0.1 *N*) HClO_4 and NH_4OH ; 0.001 *M* EDTA.

Performance of Work

Prepare two or three series of any of the following solutions with a specific activity of 4×10^5 cpm/ml:

(1) 0.5 *M* relative to NH_4Cl and a varying concentration (0.5-5.5 *M*) of CH_3COOH (at a constant pH = 3.0), containing Pu^{III} ;

(2) 0.5 *M* relative to NH_4Cl and 0.0001 *M* relative to nitriletriacetic acid with a varying pH from 1 to 3, containing Pu^{III} ;

(3) 0.5 *M* relative to NH_4Cl and a varying concentration relative to CH_3COOH ranging from 0.5 to 15 *M* (pH = 1), containing Pu^{IV} ;

(4) 0.05 *M* relative to NH_4Cl and 0.001 *M* relative to EDTA with a varying pH from 3.5 to 5.0, containing Pu^{V} .

Prepare the initial solutions containing plutonium in one of its oxidation states as described in Experiment 15.1.

Determine the distribution coefficients of Pu^{III} , Pu^{IV} , and Pu^{V} in the chosen systems according to the procedure indicated in Experiment 14.6.

Determine the composition and stability constants of the formed plutonium complexes in the studied system as described in Experiment 14.7C.

Experiment 15.8. PREPARATION OF SOME SIMPLE AND COMPLEX COMPOUNDS OF Pu [3, 16]

The experiment is performed in a class II or III laboratory in a sealed fume cupboard or a glove box.

Equipment and Reagents

Equipment and Utensils. A counter with a scintillation detector of α -radiation. A liquid proportioner. A centrifuge. A water bath. A transparent thermoplastic (Plexiglas) rack with openings for test tubes. Glass test tubes for 10 ml (15). A capillary pipette for 2-5 ml. Conical and measuring flasks for 50-100 ml (4). Chemical beakers for 100 ml. Stainless steel supports. A quartz beaker for 20-30 ml.

Radioactive Substances. A 1 *N* solution (25-30 ml) relative to HNO_3 containing ~ 0.02 mol/litre of Pu^{IV} .

Reagents. Oxalic acid. $(\text{NH}_4)_2\text{C}_2\text{O}_4$. K_2CO_3 . $(\text{NH}_4)_2\text{CO}_3$. Na_2CO_3 . NaNO_3 . CH_3COONa . CH_3COOH . $\text{Ba}(\text{NO}_3)_2$. Ethanol (80%). Solutions: 2 *N* NaOH and KOH; concentrated NH_4OH ; concentrated and 10-15% $(\text{NH}_4)_2\text{CO}_3$; 0.5 *N*, 2 *N*, 3-4 *M*, and concentrated HNO_3 ; 4% $(\text{NH}_4)_2\text{C}_2\text{O}_4$; 1 *M* $\text{Na}_2\text{C}_2\text{O}_4$; 5% NH_4NO_3 . Mixed solutions: 0.5 *N* relative to HNO_3 and 2% relative to $\text{H}_2\text{C}_2\text{O}_4$; 1.5 *N* HNO_3 .

Performance of Work

(a) Preparation of Hydroxides

Prepare consecutively in each of three test tubes 4-5 ml of a 1 *N* solution relative to HNO_3 containing ~ 0.01 mol/litre of plutonium in the oxidation states +3, +4, and +6, respectively, as described in Experiment 15.1. Heat the solution containing Pu^{IV} on the water bath to 70-80 °C. Add a concentrated solution of NH_4OH (or 2 *N* NaOH) to the obtained solutions dropwise with stirring up to $\text{pH} \geq 8-10$. Observe the precipitation of plutonium hydroxides in different oxidation states, their form (amorphous or crystalline), and colour.

(b) Preparation of Oxalates

Prepare consecutively in each of three test tubes 4-5 ml of a 1 *N* solution relative to HNO_3 containing about 0.01 mol/litre of plutonium in the oxidation states +3, +4, and +6, respectively (see Experiment 15.1). Add finely ground $\text{H}_2\text{C}_2\text{O}_4$ (or ammonium oxalate) to the solutions in small portions with vigorous stirring until the solutions become decolourized. Observe the formation of precipitates of plutonium oxalates in various oxidation states, their form (amorphous or crystalline), and colour.

(c) Carbonate Complex of Pu^{V}

Prepare 10-15 ml of a nitric acid solution containing 1-2 g/litre of Pu^{V} with a pH of 4-5 in the quartz beaker (see Experiment 15.1C). Add the carbonate of NH_4^+ , K^+ , or Na^+ (M) to the solution in accordance with the stoichiometric equation. Observe the formation of a compound with the general formula $(\text{M})_x\text{PuO}_2(\text{CO}_3)_y \cdot n\text{H}_2\text{O}$, its nature (amorphous or crystalline), and colour.

(d) Ammonium Plutonyl Tricarbonate

Prepare 4-5 ml of a 0.1-0.5 *N* solution relative to HNO_3 containing about 0.01 mol/litre of Pu^{VI} (see Experiment 15.1). Add solid $(\text{NH}_4)_2\text{CO}_3$ to the solution in small portions with

stirring until the solution decolourizes. Observe the formation of a precipitate of $(\text{NH}_4)_4[\text{PuO}_2(\text{CO}_3)_3]$, its nature (amorphous or crystalline), and colour.

(e) Sodium Plutonyl Triacetate

Prepare 4-5 ml of a 0.2 *N* solution relative to HNO_3 containing about 0.01 mol/litre of Pu^{VI} in a test tube (see Experiment 15.1). Add in accordance with calculations: CH_3COOH up to 0.6 *M*, CH_3COONa up to 0.2 *M*, and NaNO_3 up to 5-6 *M*. Stir the solution and observe the formation of a precipitate of $\text{Na}[\text{PuO}_2(\text{CH}_3\text{COO})_3]$, its nature (amorphous or crystalline), and colour.

(f) Preparation of Compound of Pu^{VII}

Obtain an approximately 0.1 *M* solution of Pu^{VII} (4-5 ml) in 2 *M* NaOH in a test tube by ozonizing for 3-4 h (see Experiment 15.1E). Next dilute the solution with water about two times and add 0.1 *M* $\text{Ba}(\text{NO}_3)_2$ so that its final concentration will not exceed the solubility of $\text{Ba}(\text{OH})_2$ in the mother liquor. Observe the precipitation of $\text{Ba}_3(\text{PuO}_5)_2 \cdot n\text{H}_2\text{O}$, its form (amorphous or crystalline), and colour.

**Experiment 15.9. SEPARATION OF U, Pu,
AND FP BY THE COPRECIPITATION METHOD [1, 9, 17]**

The problem of separating U, Pu, and their fission products (FP) by the coprecipitation method consists in providing conditions in which the metals are in different oxidation states and some of them are separated with a carrier, whereas the others remain in the solution. In a number of variants of the method (lanthanum-sulphate, lanthanum-fluoride, bismuth-phosphate, butylrhodamine-nitrate, etc.), the carrier is introduced from outside. On the other hand, upon the precipitation, for example, of carbonates and acetates, the uranium itself is the carrier.

A. LANTHANUM-SULPHATE METHOD

The essence of the method consists in the coprecipitation of Pu^{III} , Pu^{IV} , and a number of FP with a precipitate of $\text{K}_3\text{La}(\text{SO}_4)_3$ in the medium of a reducing agent with the

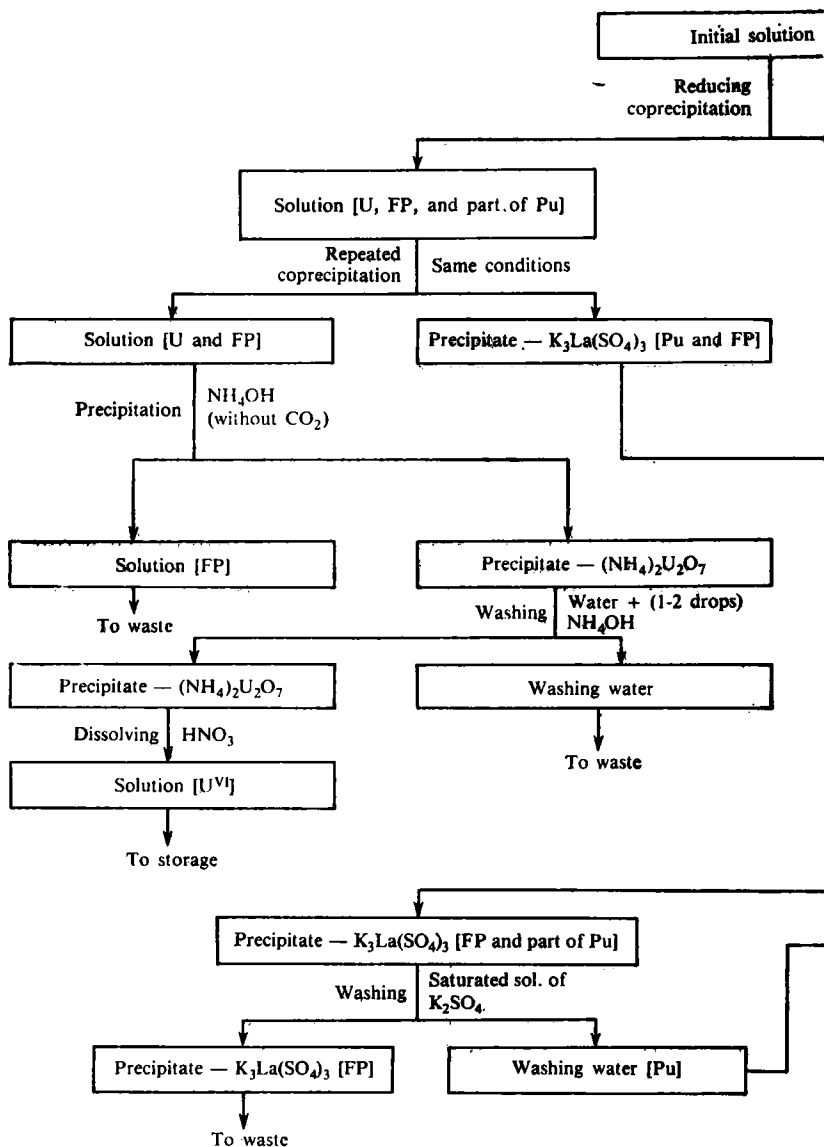
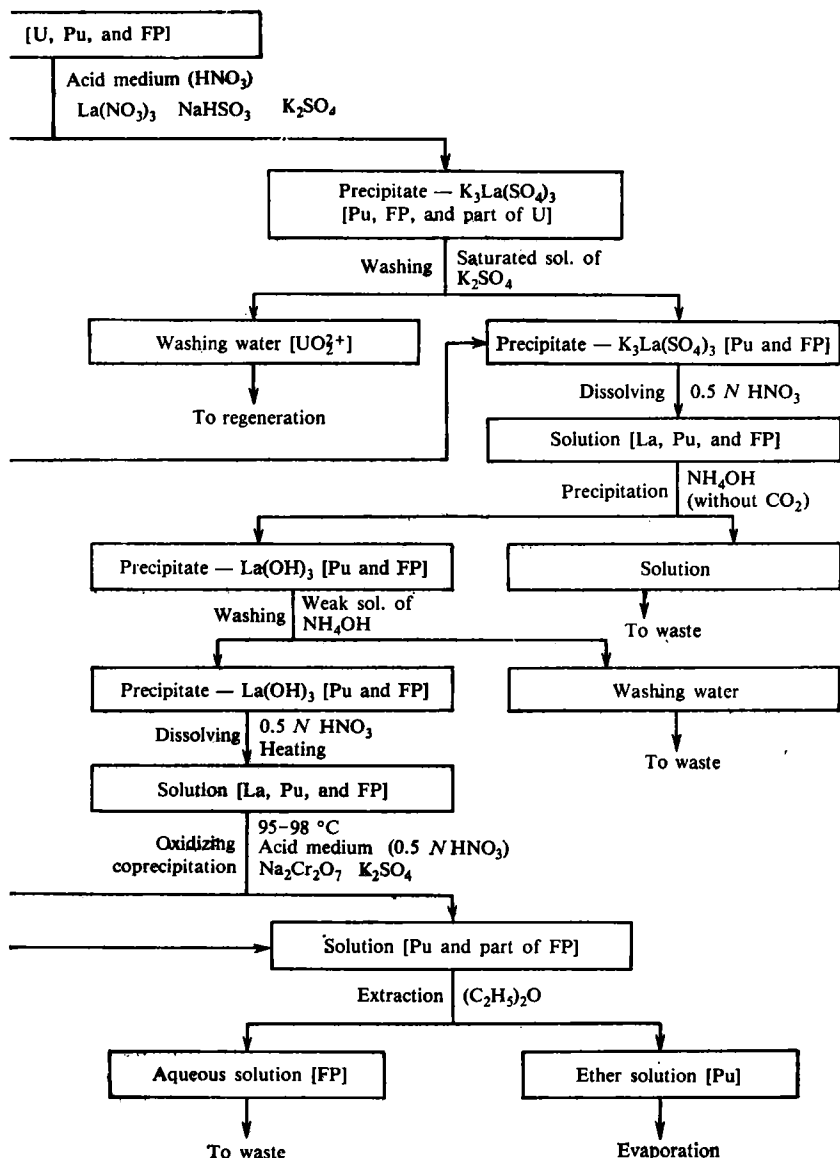


Fig. 15.2. Diagram showing the separation of U, Pu, and FP



by the lanthanum-sulphate method

following dissolving and precipitation of the lanthanum (in the form of the double sulphate) and the fission fragments in the medium of an oxidizing agent.

Equipment and Reagents

Equipment and Utensils. A counter with a scintillation detector of α -radiation. A lamp for evaporation. A water bath. A centrifuge. Beakers of thermoresistant glass for 150 ml (5). Pipettes for 10 ml with 0.1 ml graduations (3). A Büchner filter with a glass filter No. 3.

Radioactive Substances. A solution (~ 20 ml) of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (10 mg of U/ml). A solution of plutonium nitrate (2-3 ml), 1 *N* relative to HNO_3 , with a specific activity of $\sim 10^6$ cpm/ml. A 1 *N* solution relative to HNO_3 (2-3 ml) containing FP— ^{89}Sr , ^{137}Cs , ^{144}Ce , with a specific activity of $\sim 10^6$ cpm/ml.

Reagents. SO_2 (in a cylinder) or an aqueous solution of NaHSO_3 . $\text{La}(\text{NO}_3)_3$. K_2SO_4 . K_2CrO_4 . $\text{K}_4[\text{Fe}(\text{CN})_6]$. Diethyl ether. Solutions: 0.5 *N* and concentrated HNO_3 ; 5% NaOH ; concentrated NH_4OH without CO_2 .

Performance of Work

Perform the work in accordance with the diagram in Fig. 15.2.

Prepare 20 ml of a solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (10 mg of U/ml) containing plutonium nitrate with a specific activity of $\sim 10^6$ cpm/ml and indicator amounts of one or two radioactive isotopes—fission products.

To carry out the reduction process, add to the solution 1.5 ml of concentrated nitric acid, $\text{La}(\text{NO}_3)_3$ (~ 6 mg reduced to La), and an aqueous solution of NaHSO_3 up to a concentration of 0.3-0.5 *M*. Next saturate the solution with powdered K_2SO_4 (at 20 °C) while stirring with a mixer.

After 12-24 h, separate the precipitate of $\text{K}_3\text{La}(\text{SO}_4)_3$ by centrifuging or filtration through a glass porous filter (No. 3), and wash with a saturated solution of K_2SO_4 up to a negative reaction to the uranyl ion in the washing water {a reaction with $\text{K}_4[\text{Fe}(\text{CN})_6]$ in an acid medium}. Preserve the precipitate (first) for following operations.

Add a new portion of $\text{La}(\text{NO}_3)_3$ (6 mg when reduced to La) to the solution after separation of the precipitate, and keep the solution together with the formed precipitate for 12-24 h. After this, separate the precipitate (second), wash it, and combine it with the first precipitate. Repeat the precipitation once more, combine the precipitate of

$K_3La(SO_4)_3$ with the preceding ones, and preserve for further separation steps.

The solution contains uranyl nitrate and sulphate and an insignificant admixture of fission products. For additional purification from the fission products (mainly from cesium), precipitate ammonium diuranate two times. To do this, gradually add a concentrated solution of NH_4OH containing no CO_2 to the heated solution combined with all the washing water (up to the appearance of an odour). In 20-30 min, separate the ammonium diuranate precipitate by centrifuging or filtration and wash it two or three times with water containing a few drops of NH_4OH . Dissolve the ammonium diuranate in 1-2 *M* nitric acid and hand in the solution for storage.

Dissolve the combined precipitate of $K_3La(SO_4)_3$ containing plutonium and a number of fission products with heating in 0.5 *N* nitric acid, and add a small surplus of a 1 *N* solution of NH_4OH to the solution. Separate the precipitate of $La(OH)_3$ by centrifuging or filtration, wash it with a weak solution of NH_4OH , and dissolve it in a small amount of 0.5 *N* nitric acid. Reprecipitate the hydroxide twice. Bring the acidity of the final solution containing La, Pu, and FP up to 0.5 *N* relative to HNO_3 , and after heating it to 95-98 °C, add to it $Na_2Cr_2O_7$ (in an amount corresponding to 10 g/litre). After one hour, saturate the cooled solution, as previously, with K_2SO_4 . In 10-12 h, separate the precipitate of $K_3La(SO_4)_3$ from the solution and wash it. Hand in the precipitate for burial, and extract Pu^{VI} from the solution four times with 5-ml portions of diethyl ether. Evaporate the combined extract, and then dry it and measure the α -activity of the preparation obtained.

B. LANTHANUM-FLUORIDE METHOD

The method is based on the coprecipitation of Pu^{III} , Pu^{IV} , and many fission products (FP) with LaF_3 in an oxidizing medium and separating the LaF_3 and the FP.

Equipment and Reagents

Equipment and Utensils. A counter with a scintillation detector of α -radiation. A centrifuge. A water bath. An infrared lamp for evaporation. A crucible furnace for 800-1000 °C. Glass beakers. A pipette

for 10 ml with 0.1 ml graduations. Pipettes for 1 ml (paraffin-coated). Polyethylene utensils.

Radioactive Substances. A solution (~ 20 ml) of $\text{UO}_2(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ (10 mg of U/ml). A solution of plutonium nitrate (2-3 ml) with a specific activity of $\sim 10^6$ cpm/ml. A solution (2-3 ml), 1 *N* relative to HNO_3 , containing ^{89}Sr , ^{137}Cs , ^{144}Ce and having a specific activity of $\sim 10^6$ cpm/ml.

Reagents. $\text{Na}_2\text{Cr}_2\text{O}_7$. $\text{La}(\text{NO}_3)_3$. $\text{K}_4[\text{Fe}(\text{CN})_6]$. Diethyl ether. Solutions: 0.5 *N* and concentrated HNO_3 ; concentrated H_2F_2 ; NaHSO_3 ; concentrated NH_4OH (without CO_2); 10% SnCl_2 ; 5% NaOH .

Performance of Work

To 20 ml of a solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (~ 10 mg/ml) containing plutonium nitrate with a specific activity of $\sim 10^5$ cpm/ml add one or two radioactive isotopes—fission products in tracer amounts.

Add to the solution 1.5 ml of concentrated nitric acid, $\text{La}(\text{NO}_3)_3$ (~ 6 mg reduced to La) and an aqueous solution of NaHSO_3 to a concentration of 0.3-0.5 *M*. Next pour in 1 ml of hydrofluoric acid while stirring. After settling for at least six hours, separate the precipitate of LaF_3 by centrifuging or filtration. (Use polyethylene or paraffin-coated utensils when performing these operations.) Wash the precipitate (first) with water containing one or two drops of H_2F_2 up to a negative reaction of the washing water to UO_2^{2+} with $\text{K}_4[\text{Fe}(\text{CN})_6]$ in an acid medium and keep it. After separating the precipitate of LaF_3 , introduce $\text{La}(\text{NO}_3)_3$ (~ 6 mg reduced to La) into the solution with stirring. In 6-24 h, separate the second precipitate of LaF_3 , wash it, combine it with the first one and retain for following separation steps.

Use the combined solution and washing water containing UO_2^{2+} to separate the uranium from the fission products. To do this, add 2 ml of a 10% solution of freshly prepared SnCl_2 and stir the solution during 20-30 min. Separate the precipitate of uranium tetrafluoride by centrifuging or filtration and wash it with water slightly acidified with hydrofluoric acid. Check the solution for the completeness of reducing U^{VI} to U^{IV} {test for the absence of UO_2^{2+} with $\text{K}_4[\text{Fe}(\text{CN})_6]$ in an acid medium}. Subject the washed precipitate in a platinum bowl to alkaline boiling. For this purpose, heat the precipitate with 5-7 ml of a 5% solution of NaOH on a boiling water bath during 1.5-2 h.

Also subject the precipitate of LaF_3 containing plutonium

and fission products forming insoluble fluorides to alkaline boiling in the same conditions as above. Alkaline boiling may be replaced with treatment of the precipitate with a mixture of acids: H_3BO_3 and HNO_3 . After alkaline boiling, a precipitate of $\text{La}(\text{OH})_3$ is obtained together with hydroxides of plutonium and certain fission products.

Separate the hydroxides by centrifuging or filtration, wash them with a dilute solution of NaOH (up to a negative reaction for the F^- ion) and dissolve them with heating in 25 ml of 0.5 N nitric acid. After this, add 0.25-0.30 g of sodium bichromate to the solution and heat the mixture at 95-98 °C during one hour. Add 1 ml of a concentrated solution of H_2F_2 to the cooled solution. After several hours, separate the precipitate of LaF_3 from the solution and hand it in for burial. Extract the plutonium contained in the solution with diethyl ether. Evaporate the ether solution. Determine the plutonium content according to the α -activity by the radiometric method.

Dissolve the precipitate of $\text{U}(\text{OH})_4$ obtained after alkaline boiling in nitric acid. Bring the solution up to an acidity of 0.5 N relative to the HNO_3 , add 1 g of $\text{Na}_2\text{Cr}_2\text{O}_7$ to it, and heat at 95-98 °C during one hour. After cooling the solution, add dropwise a concentrated (without CO_2) solution of NH_4OH up to a weak odour. After settling of the precipitate of $(\text{NH}_4)_2\text{U}_2\text{O}_7$, separate it by centrifuging or filtration and wash it with water (4-5 ml) containing a few drops of NH_4OH . Dry the precipitate and roast it at 800-1000 °C during two hours, cool it, and weigh it in the form of U_3O_8 . Hand in the uranous-uranic oxide for storage.

Compile a diagram showing the separation of uranium, plutonium, and their fission products (FP) by the lanthanide-fluoride method (according to the diagram in Fig. 15.2).

**Experiment 15.10. SEPARATION OF U, Np, Pu,
AND FP BY EXTRACTION WITH TRIBUTYLPHOSPHATE
AND AMINES [1, 7, 17, 18]**

The separation of U, Np, Pu, and FP with the aid of TBP and amines is possible because the nitrates of these elements form complexes with them that differ in their stability.

Equipment and Reagents

Equipment and Utensils. A counting installation with a scintillation detector of α -radiation or an end-window counter. A water bath. A liquid proportioner. A vibrator controlled with the aid of an auto-transformer. A separatory funnel for 25-30 ml. Glass or quartz test tubes for 20-25 ml (4). A capillary pipette for 2-5 ml. A calibrated pipette with a syringe. Conical and measuring flasks for 50-100 ml (4).

Radioactive Substances. A solution (15-20 ml) of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (5-10 ml of U per ml). A 1 *N* solution (2-5 ml) relative to HNO_3 containing ^{239}Np and ^{239}Pu with a specific activity of $\sim 10^6$ cpm/ml. A 1 *N* solution (2-3 ml) relative to HNO_3 containing ^{89}Sr , ^{144}Ce , and ^{106}Ru with a specific activity of $\approx 10^6$ cpm/ml.

Reagents. NH_4NO_3 . NaBiO_3 . $\text{K}_2\text{Cr}_2\text{O}_7$. $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$. Mohr's salt $(\text{NH}_2\text{SO}_2)_2\text{Fe}$. Solutions: 3-4 *M* HNO_3 ; 30% TBP in kerosene; mixed—0.05 *M* relative to NaNO_2 , 0.5 *N* relative to HNO_3 , and 6 *M* relative to NH_4NO_3 ; mixed—0.5 *N* relative to HNO_3 and 4 *M* relative to NH_4NO_3 ; 40% $(\text{NH}_4)_2\text{SO}_4$ or 10-20% $(\text{NH}_4)_2\text{CO}_3$; 0.2 *M* tri-*n*-octylamine (TOA) or tri-*iso*-octylamine.

Performance of Work

Perform the work in accordance with the diagram shown in Fig. 15.3.

Prepare in a test tube 10-15 ml of a solution, 1 *N* relative to HNO_3 and 6 *M* relative to NH_4NO_3 containing uranyl nitrate (5-10 mg of U per ml) and tracer amounts of ^{233}U , ^{239}Np , ^{239}Pu , ^{89}Sr , ^{144}Ce and ^{106}Ru (with an activity each of $\sim 10^5$ cpm/ml). Oxidize the neptunium and plutonium to an oxidation state of +6 by adding NaBiO_3 to the solution in the cold up to the formation of a suspension or by heating the solution with $\text{K}_2\text{Cr}_2\text{O}_7$ (5-10 g/litre) on the water bath at 90-95 °C during one hour. Transfer the solution into the 25-30-ml separatory funnel and extract the U^{VI} , Np^{VI} , and Pu^{VI} with a 30% solution of TBP using a ratio of the volumes of the aqueous and organic phases equal to 3 : 1 and shaking the mixture during five minutes at room temperature. Repeat this operation.

For additional purification of the actinides, wash the organic phase two or three times with a half volume of 3-4 *M* nitric acid. Next reextract the neptunium from the organic phase by washing it two or three times during 5-10 min with an equal volume of a solution having the composition 0.05 *M* relative to NaNO_2 , 0.5 *N* relative to HNO_3 , and 6 *M* relative to NH_4NO_3 . In these conditions, the Np^{VI} is reduced to the form Np^{V} that is not extracted, while the plutonium passes into a state with the oxidation

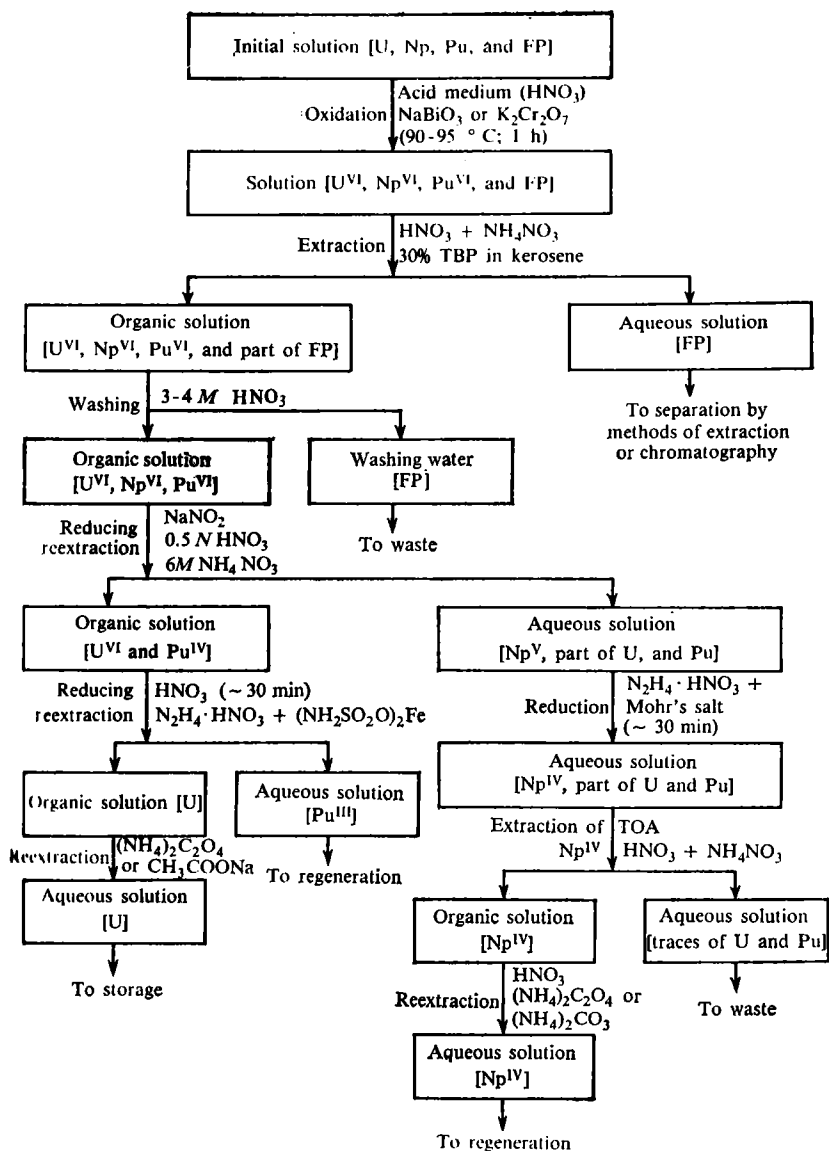


Fig. 15.3. Diagram showing the separation of U, Np, Pu, and FP with the aid of TBP and amines

number +4 and is not reextracted. Retain the organic phase for the following separation steps.

For completing its purification, reduce the neptunium in the cold with the aid of hydrazine nitrate (0.2 mol/litre) in the presence of Mohr's salt (~ 0.1 mol/litre) during 30 min, and then extract the Np^{IV} with a 0.2 *M* solution of tri-*n*-octylamine (TOA) or tri-*iso*-octylamine from a solution having the composition 0.5 *N* relative to HNO_3 and 4 *M* relative to NH_4NO_3 . Extract the Np compound from the TOA with a solution of 0.1-0.5 *N* relative to HNO_3 in the presence of complexing substances, for example $(\text{NH}_4)_2\text{C}_2\text{O}_4$ (4%) or $(\text{NH}_4)_2\text{CO}_3$ (10-20%).

Reextract the plutonium(III) from the organic phase of TBP by treatment with a 0.2 *N* solution relative to HNO_3 in the presence of the reducing agent $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$ (0.2-0.3 mol/litre) with the addition of freshly prepared iron(II) sulphamate (0.05 mol/litre). Perform the treatment during 30 min at $V_{\text{org}}/V_{\text{aq}} = 2.5$.

After extracting the neptunium and plutonium, use the organic phase for reextraction of the uranium. For this purpose, wash the solution (3 or 4 times) in an organic solvent with half the volume of one of the following solutions: 0.3 *M* $(\text{NH}_4)_2\text{C}_2\text{O}_4$, 1 *M* CH_3COONa , or 1.5 *M* Na_2CO_3 .

In the course of the extraction separation, take aliquot parts from the organic and aqueous phases (0.09 ml each) for measuring the α - or β -activity and determine the amount of isotope extracted and reextracted by the corresponding solutions (in %).

**Experiment 15.11. SEPARATION OF U, Np, Pu,
AND FP BY EXTRACTION OF THEIR INTRACOMPLEX
COMPOUNDS WITH N-BENZOYLPHENYLHYDROXYLAMINE
[1, 12, 17]**

Actinides in the +4 oxidation state form much more stable intracomplex compounds with N-benzoylphenylhydroxylamine (BPHA) than in the +3 or +6 oxidation state. It is exactly this difference in their chemical behaviour that underlies the extraction method of separating U, Np, and Pu and separating them from the fission-product elements.

Equipment and Reagents

Equipment and Utensils. A counting installation with a scintillation detector of α -radiation or an end-window counter. A water bath. A liquid proportioner. A separatory funnel for 25-30 ml. Glass or quartz test tubes for 20-25 ml (4). A capillary pipette for 2-5 ml. A calibrated pipette with a syringe. Conical and measuring flasks for 50-100 ml (4).

Radioactive Substances. A solution (10-15 ml) of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2-5 mg of U per ml). A 1 *N* solution (2-3 ml) relative to HNO_3 containing ^{239}Np and ^{239}Pu with a specific activity of $\sim 10^6$ cpm/ml. A 1 *N* solution (2-3 ml) relative to HNO_3 , containing ^{144}Ce and ^{95}Zr with a specific activity of $\sim 10^6$ cpm/ml.

Reagents. NaNO_2 . CHCl_3 . NH_2OH . HCl . FeCl_3 . Mohr's salt. Solutions: 0.4 *M* *N*-benzoylphenylhydroxylamine; 3.5 *M* H_2SO_4 ; 1 *N* and 6 *M* HNO_3 ; 30% TBP.

Performance of Work

Perform the work in accordance with the diagram in Fig. 15.4.

Prepare in a test tube 10-15 ml of an initial 2 *N* solution relative to HNO_3 containing uranyl nitrate (2-5 mg of U per ml) and tracer amounts of a mixture of ^{233}U , ^{239}Np , ^{239}Pu , ^{144}Ce , and ^{95}Zr . Introduce the isotopes into the solution in amounts such that their specific activity will be $5 \times 10^4 - 1 \times 10^5$ cpm/ml.

To transfer the plutonium and neptunium into the +4 and +5 oxidation states, respectively, heat the solution in the presence of NaNO_2 (0.05 mol/litre) in a test tube on the water bath during 15-20 min. Transfer the cooled solution with the aid of the pipette into the separatory funnel and extract the Pu^{IV} and Zr^{IV} with an equal volume of a 0.4 *M* solution of *N*-BPHA in CHCl_3 with shaking during one minute, after which separate the phases. In these conditions, the U^{VI} , Np^{V} , and Ce^{III} are not extracted, and they are thus separated from the Pu^{IV} and Zr^{IV} . Reextract the Pu^{IV} from the organic phase by shaking during 3 min with a 3.5 *M* solution of H_2SO_4 (with a ratio of the volume of $V_{\text{org}}/V_{\text{aq}} = 2.5$) and thus separate it from the Zr^{IV} remaining in the organic phase.

Consecutively treat the aqueous phase (2 *N* relative to HNO_3) with hydroxylamine chloride (0.4 mol/litre), FeCl_3 (0.2 mol/litre), and a solution containing 0.1 mol/litre of Mohr's salt (for reducing the Np^{V} to Np^{IV}). Next extract the Np^{IV} with an equal volume of a 0.4 *M* solution of

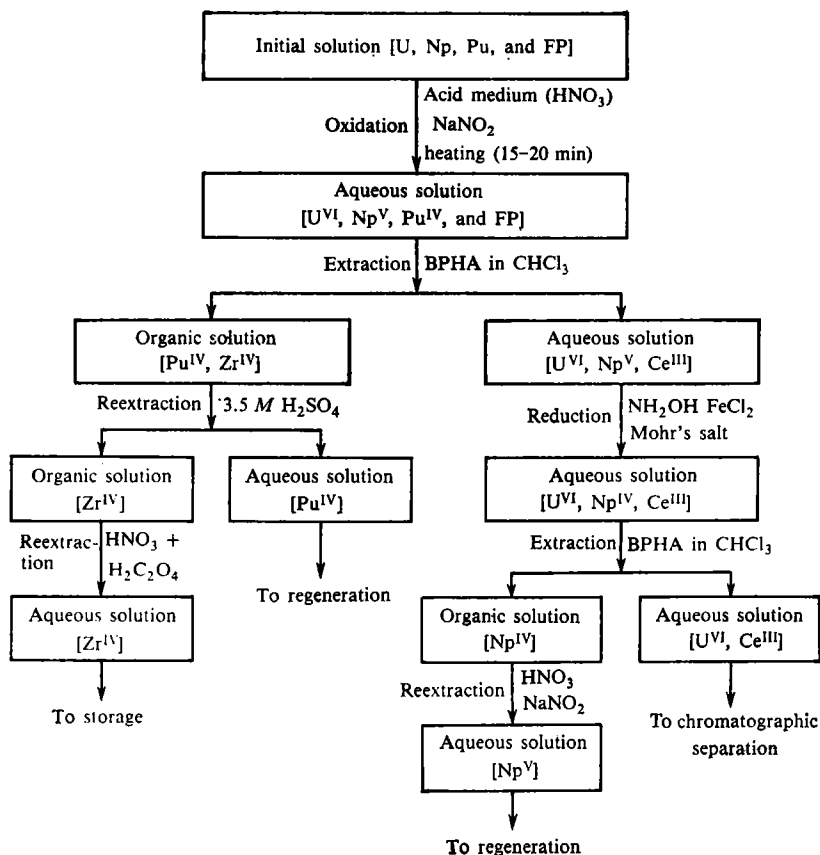


Fig. 15.4. Diagram showing the separation of U, Np, Pu, and FP with the aid of BPHA

BPHA in chloroform with shaking during 5 min. Separate the U^{VI} and Ce^{III} remaining in the aqueous phase by the chromatographic method (see Experiment 15.12), employing consecutive washing out of the uranium with 1 *N* nitric acid, and the cerium with 5-6 *M* nitric acid or extraction of the uranium with a 30% solution of TBP.

Extract the neptunium from the organic phase by washing it (2-3 times) with small portions of a 2 *N* solution relative to HNO_3 containing ~ 0.1 mol/litre of $NaNO_2$.

In the course of the extraction process of separating the mixture of radioelements, take aliquot parts (0.09 ml each) from the organic and aqueous phases for measuring the α - or β -activity. Determine the extraction of the relevant element (in %). With chromatographic separation, obtain elution curves.

Experiment 15.12. SEPARATION OF U, Np, AND Pu BY THE ION-EXCHANGE METHOD [1, 17-19]

The ability of metal-containing ions (in indicator amounts) to be adsorbed in small columns from quite considerable volumes of a dilute acid solution is used for their concentration. The desorption of an element with cation exchangers is achieved by the selective elution with moderately concentrated solutions of HCl or HNO₃, and also with solutions of various complexing agents such as the anions of citric, lactic, α -hydroxy-*iso*-butyric and ethylenediamine-tetraacetic acids.

The sequence of desorption from the resin of elements in different oxidation states is different. For example, for plutonium it is as follows: $+5 > +6 > +3 > +4$, i.e. is the reverse of the order in which differently charged ions of the metals are adsorbed.

Equipment and Reagents

Equipment and Utensils. A counting installation with a scintillation detector of α -radiation or an end-window counter. A water bath. A liquid proportioner. A rotary collector. A chromatographic column (6-10 cm high and ~ 0.5 cm in diameter). Glass test tubes for 10 ml (15). Chemical beakers for 20-30 ml. Measuring and conical flasks for 50-100 ml (4). A capillary pipette for 3-5 ml.

Radioactive Substances. A solution (15-20 ml) of UO₂(NO₃)₂·6H₂O (5-10 mg of U per ml). A 1 *N* solution (1-2 ml) relative to HNO₃ containing ²³⁹Np and ²³⁹Pu with a specific activity of $\sim 10^6$ cpm/ml. A 1 *N* solution (1-2 ml) relative to HNO₃ containing 0.005 mol/litre of ²³⁷Np V.

Reagents. N₂H₄·HNO₃. Mohr's salt. Cation exchanger KU-2 (grain size 0.25-0.30 mm) or SM-12. KBrO₃. Solutions: 0.4, 0.6 *N* and 4-6 *M* HNO₃; mixed—6 *M* relative to HNO₃ and 0.3 *M* relative to NH₂SO₂OH; 5-6 *M* acetic acid; 0.5% oxalic; 0.5% citric; 0.5 *M* lactic; 0.5 *M* glycolic or 0.3 *M* α -hydroxy-*iso*-butyric; 1.5×10^{-4} *M* diethylenetriaminepentaacetic acid.

Performance of Work

Prepare in a test tube 15-20 ml of an initial 0.5 *N* solution relative to HNO_3 containing uranyl nitrate (5-10 mg of U per ml) and tracer amounts of ^{233}U , ^{239}Np , and ^{239}Pu (with a specific activity of 5×10^4 - 1×10^5 cpm/ml). (If no isotope ^{239}Np is available, the long-lived isotope ^{237}Np may be used.)

To transfer the plutonium and neptunium into a state with the oxidation numbers +3 and +4, respectively, first heat the solution in the presence of $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$ (0.2-0.3 mol/litre) on the water bath at 80-90°C during 30 min, and then after adding Mohr's salt (0.1 mol/litre) keep it in the cold (10-15 min). Pass the solution through a chromatographic column filled with the cation exchanger KU-2 in the H^+ form. Choose such a rate of filtration that the duration of contact of the solution with the resin will be at least one hour.

Desorb the U^{VI} by washing the column with 0.4 *N* nitric acid and determine the uranium content in small fractions (5-10 ml each) by the radiometric method with the use of the isotope ^{233}U added to the initial solution as a radioactive indicator.

The Np and Pu can be separated according to one of the following two variants.

Consecutively desorb the Np^{IV} by washing the column with a 0.5% solution of citric acid at a pH of 2.8-3.0 and the Pu^{III} with a solution of 6 *M* relative to HNO_3 and 0.3 *M* relative to sulphaminic acid. When washing the column with a solution of citric acid, the Np^{IV} should mainly be washed out, while the Pu^{III} remains on the resin. Solutions of acids such as 5-6 *M* acetic (at pH = 3.0), 0.5% oxalic, 0.5 *M* lactic (at pH = 2.5-3.0), 0.5 *M* glycolic (at pH = 2.5), 0.3 *M* α -hydroxy-*iso*-butyric (at pH = 4.0), and 1.5×10^{-4} *M* diethylenetriaminepentaacetic acid (at pH = 1.0) may also be used as eluents for the Pu^{III} .

The neptunium is desorbed by washing the column with a 0.4 *N* solution of HNO_3 in the presence of a mild oxidizing agent, for example 0.1 mol/litre of KBrO_3 . In the given case, the separation of the mixture is based on the displacement of the Np^{V} and Np^{VI} from the resin, whereas the Pu^{IV} remains completely sorbed. Next the Pu^{IV} is desorbed with a 4-6 *M* solution of HNO_3 .

In the process of desorbing the neptunium and plutonium, determine their content in the individual fractions. After completion of the separation stage, plot curves of the measured α - or β -activity of the fractions against the number of passed eluent volumes (take the volume of the swollen sorbent in the column as the volume unit).

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Part IV The Use of Radioactive Isotopes in Chemical Research

The method of radioactive indicators (tracers) acquired a great significance in many fields of science. It is used on an especially large scale in biology and medicine. Radioactive isotopes have found a widespread application when studying a number of very important problems in chemistry and physics. To date, the results of investigations are known involving the use of radioactive isotopes in studying the structure of molecules and the reactivity of atoms in molecules, in investigating the kinetics and mechanism of chemical reactions, the mechanism of catalysis, adsorption, diffusion, and evaporation, for analysis, in electrochemistry, and so on. Radioactive isotopes are also employed for investigating and monitoring industrial processes.

When performing investigations by the method of radioactive tracers, one must obtain a radioactive isotope by one of the known methods and separate it in a chemically and radiochemically pure state. Next one must synthesize the compound needed for the investigation. In the majority of cases, the required isotope can be purchased, and in a number of cases the compound too, produced by the industry.

To ensure safety in work, it is desirable to use a minimum amount of the radioactive substance, which is calculated proceeding from the conditions of the experiment.

The amount A of a radioactive isotope in Bq needed for running an experiment whose results are determined according to the radioactivity of the sample taken for measure-

ment can be evaluated by the formula

$$A = I \frac{m_0}{m} \frac{100}{p} \frac{100}{\varphi}$$

where I is the activity of the sample that can be measured with the given accuracy, cps, m_0 and m are the mass of the substance being investigated and the sample taken for measurement, respectively, p is the fraction of the radioactive isotope that gets into the substance being investigated, %, and φ is the radiation registering coefficient, %.

Before beginning to run an experiment with a radioactive isotope, one must determine the conditions of the experiment from the viewpoint of its safety, then run a "cold" experiment (without the radioactive isotopes) that as far as possible reproduces the sequence of operations when working with the radioactive substance.

Since the radioactive substance taken for investigation has a specific activity other than that needed for performing the experiment, it is diluted with the same non-radioactive compound (carrier) to the required specific activity. The calculations are performed with a view to the fact that the sample taken in the last operation must have an activity that can be measured in the available counter with the given accuracy—200-5000 cpm (see Introductory Work—Vol. 1, p. 58).

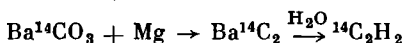
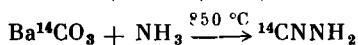
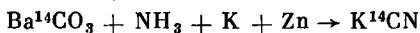
If an experiment is being performed with a mixture of radioactive isotopes of a given element, part of the initial substance is to be retained as a "witness" with which the activity of the specimens obtained as a result of the experiment and measured simultaneously with the witness is compared. The amount of substance in the witness must be known.

When measuring the activity, one must observe all the conditions that make it possible to obtain the most accurate results. These conditions include the use of the same stably operating apparatus and counter, which is controlled by measuring the activity of standard specimens before and after measuring preparations; an identical geometrical position of the samples relative to the detector in measurements; account of secondary phenomena (reflection, absorption, and self-absorption); account of measurement errors; and the preparation of specimens for measuring the radioactivity of an isotope from the same substance.

Chapter 16 The Synthesis and Analysis of Labelled Compounds [1]

Labelled compounds are prepared by direct chemical synthesis, synthesis with the aid of isotope exchange, "hot" synthesis, biosynthesis, radiation synthesis, etc.

Direct chemical synthesis can be used to prepare the overwhelming majority of labelled compounds needed in science and engineering. The chemical synthesis of complex labelled substances is time-consuming, however, and the yield of the products is often low. This is associated with the fact that not any compounds can be used as the initial radioactive substances, but only those that are obtained in the process of production and separation of the given isotope. For example, for the synthesis of compounds labelled with ^{14}C , the initial substance is $\text{Ba}^{14}\text{CO}_3$. It is used to prepare the following key compounds that are very important for further syntheses:



Carbon dioxide labelled with ^{14}C is used to prepare acids labelled in the carboxyl group, the reduction of these acids yields alcohols labelled in the alpha-position, then aldehydes, sugars, and plastics. Acids labelled in the alpha-position are prepared via alkyl halides from labelled alcohols by magnesium-organic synthesis. Labelled potassium cyanide is used to produce diazomethane, formic acid, and nitriles. Labelled cyanamide is the starting compound for preparing urea, thiourea, and heterocyclic compounds. Labelled acetylene is used for synthesis of aldehydes, acids and ketones, saturated and aromatic hydrocarbons.

Gaseous tritium or tritium water is the starting point for the synthesis of compounds labelled with tritium. The hydrogenation of carbon dioxide over a catalyst yields tritium-containing hydrocarbons, saturated hydrocarbons are pre-

pared from unsaturated ones, and lithium aluminium hydride is used to prepare labelled alcohols. Hydration and hydrolysis with tritium water are used to a greater extent. For example, the hydrolysis of $R-MgHal$ and $R-Zn-R'$ leads to the formation of hydrocarbons containing tritium; the reaction of tritium water vapour with acetylene over a catalyst leads to the formation of acetaldehyde.

Acetylene labelled with tritium is used to prepare benzene, toluene, naphthalene, and fluorene by pyrolytic polymerization.

The initial compound for the synthesis of compounds labelled with ^{35}S is $Ba^{35}SO_4$. In the first stage, it transforms into $Ba^{35}S$ and $H_2^{35}S$, $Na_2^{35}SO_4$, and thiourea- ^{35}S . These compounds go to prepare salts of sulphuric and hydrosulphuric acids, thiocyanides, thiosulphates, sulphamide preparations, Thiophos, sulphazole, vitamin B, etc.

The above examples show the diversity of possibilities, on the one hand, and the complicated nature (a multitude of steps) of the chemical synthesis of labelled compounds on the other.

Synthesis by isotope exchange can be used for incorporating radioactive and stable isotopes into molecules instead of atoms in a mobile position. Atoms in inorganic compounds have a high mobility, consequently a "label" can readily be incorporated into any position of a compound by isotope exchange except when it is the central atom of a complex ion. In organic compounds, atoms of the halogens, metals, and in some cases sulphur atoms are mobile. Hydrogen atoms are mobile in OH , SH , and NH groups. The $C-H$ bond is more stable, and the exchange of such hydrogen atoms is possible only in rigorous conditions (alkaline or acid media). Carbon atoms in organic compounds are stationary, but in conditions when regrouping occurs, the incorporation of radioactive carbon atoms into a molecule by isotope exchange is possible.

At present, isotope exchange is chiefly used for obtaining labelled organo-halogen and certain inorganic compounds.

"Hot" synthesis has meanwhile not found broad application. Some organo-halogen compounds are prepared by direct irradiation in a reactor. Of interest is the incorporation of ^{14}C and 3H into complicated organic molecules by means of reactions of recoil atoms. Particularly, a labelled organic compound is synthesized by the direct contact of organic

compounds with gaseous tritium— $^3\text{H}_2$ (the Wilzbach method). Owing to the radioactive decay of one of the atoms of the molecule $^3\text{H}-^3\text{H}$, the other atom acquires properties allowing it to replace a protium atom in a molecule. This method has begun to come into great favour in practice. The process is accelerated in conditions of atomization of $^3\text{H}_2$ on a heated platinum wire.

Biosynthesis, accomplished with the participation of living organisms developing on labelled substrates, leads to a radioactive isotope being in the composition of a complicated substance produced by the organism. For example, the photosynthesis by tobacco leaves of glucose, fructose, and saccharose labelled with ^{14}C in an atmosphere of radioactive carbon dioxide is one of the most effective industrial methods of preparing these compounds.

Radiation and other methods of synthesizing labelled compounds have meanwhile found no application in industry and are only being developed in laboratories.

Experiment 16.1. SYNTHESIS OF POTASSIUM CYANIDE- ^{14}C [1]



Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window counter. A tube made from heat-resistant glass (Pyrex). A muffle furnace. A dry chamber. An analytical balance.

Radioactive Substances. $\text{Ba}^{14}\text{CO}_3$ with a specific activity of 37 kBq/g (1 $\mu\text{Ci/g}$).

Reagents. Potassium (metal). NH_4Cl . Absolute diethyl ether. Ethanol. Solutions: concentrated H_2SO_4 ; titrated AgNO_3 ; dilute KOH .

Performance of Work

To a mixture of 0.2 g of barium carbonate- ^{14}C and 0.1 g of ammonium chloride placed in the Pyrex tube 17 cm long and 1.6 cm in diameter provided with constrictions on its ends, carefully add (in portions) in a nitrogen atmosphere 1-2 g of metallic potassium preliminarily cleaned of its film under a layer of absolute diethyl ether (if metallic sodium is used, the yield drops to 50%). Remove the ether in a vacuum and melt the metal. Seal the tube. Again melt the

freshly prepared platinum oxide—Adams's catalyst (obtain 0.085 g from the laboratory assistant) under atmospheric pressure. Prepare hydrogen in the Kipp gas generator by acting with hydrochloric acid on zinc containing no arsenic, and pass it through a 20% solution of KOH, a 20% solution of AgNO_3 , and a saturated solution of KMnO_4 . Perform the hydrogenation with shaking at room temperature during 4-7 h. Alkalize the reaction mixture, distil the free amine into a receiver containing hydrochloric acid, and obtain methylamine- ^{14}C chloride. When the distillate (reduce its volume to 5 ml) is heated for 30 min with a small surplus of potassium cyanate on a boiling water bath, the yield of methylamine- ^{14}C chloride is 98%. Prepare the pure product by extracting the dry reaction product with boiling absolute methanol (*be careful—methanol is poisonous!*).

(b) *N*-Nitroso-*N*-(Methyl- ^{14}C)-Urea

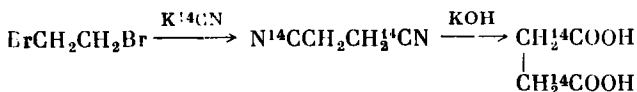
Boil a solution containing 0.24 g of the unpurified methylamine- ^{14}C chloride and 0.711 g of urea in 1 ml of water with a reflux condenser during three hours. Add 5.6 ml of an aqueous solution containing 0.79 g of methylurea (the carrier) and 1.3 g of sodium nitrite to the solution of methyl- ^{14}C urea cooled with ice while stirring it. Next add dropwise during 15 min a solution of 0.65 ml of H_2SO_4 and 7.1 g of icy water. Separate the precipitate and purify it of inorganic impurities by extraction with absolute methanol (*be careful—it is poisonous!*) at room temperature. Prepare a crystalline powder by evaporating the extracting agent. Determine the yield of the product calculated for cyanide. Find the specific activity and the radiochemical yield in the usual way.

(c) *Diazomethane- ^{14}C*

To an ice-cooled mixture of 50 ml of diethyl ether and 3 ml of a 50% solution of KOH add with stirring 1.04 g of *N*-nitroso-*N*-(methyl- ^{14}C)-urea. Connect a cooler with a prolong to the flask. Immerse the end of the prolong into the receiver below the surface of the ether poured into it and cooled by a mixture of ice and salt. The evolved gases must pass through a second similar trap. Heat the reaction mixture on a water bath at 50 °C and distil off the major

part of the ether (but not all of it). Analyse the ether solution by esterification of a definite amount of the solution with a surplus of benzoic acid and back titration with an alkali.

Experiment 16.3. SYNTHESIS OF SUCCINIC-1,4-¹⁴C₂ ACID [1]



Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window counter. A flask with a reflux condenser. An analytical balance. A separatory funnel.

Radioactive Substances. K¹⁴CN with a specific activity of 37 kBq/g (1 μCi/g).

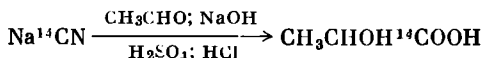
Reagents. Dibromoethane. KI. Ethanol. Diethyl ether. Chloroform. A 2.5 M solution of H₂SO₄. KOH.

Performance of Work

Add 1.61 g of ethylene bromide to a mixture of 0.616 g of potassium cyanide-¹⁴C (*be careful—it is poisonous!*), an insignificant amount of KI (a catalyst), 1 ml of water, and 3 ml of ethanol. Boil the mixture in the flask with the reflux condenser during 75 min, dilute it with 100 ml of water and extract with ether for removing the surplus dibromide. Acidify the aqueous solution with 20 ml of 2.5 M sulphuric acid and keep it at room temperature for 30 min to remove the isonitriles, which readily hydrolyze in the dilute acid with the formation of primary amines and formic acid. Separate the dinitrile by extracting the mixture with chloroform, and evaporate the extract. Without separating the unpurified dinitrile, saponify it with an alkali, and after removal of the neutral substances with ether, separate the acid by acidification and continuous extraction with ether. After drying in air, determine the melting point of the succinic acid and compare it with tabulated data.

Determine the total mass of the obtained acid. Measure its specific activity and calculate its radiochemical yield.

Experiment 16.4. SYNTHESIS OF LACTIC-1-¹⁴C ACID [2]



Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window counter. A shaker. A flask for 250 ml with a reflux condenser. A vacuum desiccator. An analytical balance. A separatory funnel.

Radioactive Substances. Na¹⁴CN with a specific activity of 37 kBq/g (1 μCi/g).

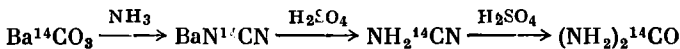
Reagents. Acetaldehyde. Absolute ethyl alcohol. Toluene. Solutions: 2.15 N H₂SO₄, HCl (density 1.18 g/cm³), 1 N and saturated NaOH.

Performance of Work

Dissolve 1 g of sodium cyanide-¹⁴C (*be careful—it is poisonous!*) in 4 ml of water. Cool the solution to 0 °C, add 10.3 ml of 2.15 N sulphuric acid (cooled with ice), 1.4 ml of acetaldehyde, and 2.0 ml of a 1 N solution of NaOH. After thorough shaking, keep the mixture at room temperature for 20 min. Add 40 ml of hydrochloric acid (with a density of 1.18 g/cm³), rapidly shake the mixture, and boil it for 6 min. Add 100 ml of water, cool the solution and neutralize it with a saturated solution of NaOH. Add a surplus of sodium hydroxide and distil the solution up to the complete removal of ammonia, after which neutralize it with sulphuric acid (*without a surplus!*). Evaporate the solution to a minimum volume.

Add 40 ml of toluene, and distil off the remaining water in the form of an azeotropic mixture. Extract the residue with three portions (50 ml each) of absolute ethyl alcohol. Distil off the solution and extract the residue with 15 ml of absolute alcohol. Remove the suspension by centrifuging and extraction with three portions (1 ml each) of absolute alcohol. Combine the extracts and remove the solvent by distillation. Dry the substance 24 hours in the vacuum desiccator. Determine the yield and the specific activity of the acid.

Experiment 16.5. SYNTHESIS OF UREA-¹⁴C [1]



Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window counter. A tubular furnace (high-temperature). A quartz tube. A platinum boat. A centrifuge. A device for drying in a vacuum. An analytical balance. A chemical beaker. A round-bottom flask. A separatory funnel.

Radioactive Substances. $\text{Ba}^{14}\text{CO}_3$ with a specific activity of 37 kBq/g (1 $\mu\text{Ci/g}$).

Reagents. NH_3 (gas). Diethyl ether. Methanol. P_2O_5 . NaOH. CaCl_2 . Solutions: concentrated— H_2SO_4 , HCl, and NH_4OH .

Performance of Work

(a) Barium Cyanamide- ^{14}C

Put a weighed sample (3.11 g) of barium carbonate- ^{14}C in a platinum boat into the quartz tube. Insert the latter into the furnace and pass dry ammonia over the boat. During three hours, bring the temperature up to 850 °C, switch off the furnace, and when the tube cools stop supplying the ammonia. As a result, barium cyanamide forms with almost a quantitative yield.

(b) Cyanamide- ^{14}C

Place the obtained barium cyanamide- ^{14}C in a beaker and pour 10 ml of water over it. While cooling on an ice bath and vigorously stirring, add dropwise cold concentrated sulphuric acid (in an amount equivalent to the barium content).

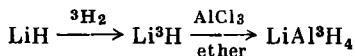
Stir the mixture another hour, keeping the pH of the medium at 5.5 (add hydrochloric acid if necessary), centrifuge, and transfer the solution into the round-bottom flask. Wash the precipitate with water. Evaporate the aqueous fractions until dry in a vacuum at a temperature not over 40 °C. Extract the residue with ether, and evaporate the ether.

To obtain pure cyanamide, dry the residue in a vacuum over phosphorus pentoxide, extract with ether, and again dry in a vacuum, first over phosphorus pentoxide, and then over sodium hydroxide. Determine the yield and melting point of the product.

(c) Urea-¹⁴C

Dissolve the cyanamide obtained in water and treat it with 1 ml of concentrated sulphuric acid. Slowly evaporate the solution at 40-60 °C until a syrupy residue is obtained. Dissolve the residue in 25 ml of water, alkalize with an NH₄OH solution and evaporate until dry at room temperature in a weak stream of air. Dry the residue in a vacuum over calcium chloride and extract the product three times with warm methanol (10 ml each time). Evaporate the alcohol, sublime the precipitate in a vacuum (1.33 Pa) at 60-70 °C. Determine the specific activity and yield of the urea.

Experiment 16.6. SYNTHESIS OF LITHIUM ALUMINIUM HYDRIDE-³H [3]



Equipment and Reagents

Equipment and Utensils. A counting installation with a 2 π flow-type counter (SOT-25-BFL). A three-neck flask with a mechanical stirrer, a mercury seal, a reflux condenser, and a dropping funnel. An analytical balance. A flask of heat-resistant glass (Pyrex). A gas meter.

Radioactive Substances. Gaseous ³H₂ (standard packing with a total activity of 37 MBq (1 mCi)).

Reagents. Diethyl ether. AlCl₃. LiAlH₄. LiH. Nitrogen (in a cylinder).

Performance of Work

(a) Lithium Hydride-³H

Prepare the product by an exchange reaction. For this purpose, heat a powder of LiH with a particle size of 0.04-0.06 mm in a tritium atmosphere at 350 °C in the Pyrex flask. If the particle size of the lithium hydride powder exceeds 0.06 mm, in the following it will react very slowly with the aluminium chloride and even boiling during a week will result in a low yield.

(b) Lithium Aluminium Hydride-³H

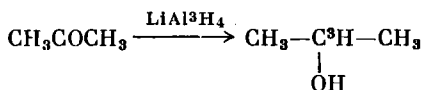
Put a solution containing 3.05 g of lithium aluminium hydride in 30 ml of diethyl ether (prepare it beforehand so that the induction period will terminate and to avoid a too

violent reaction that does not lend itself to control even upon cooling) into the three-neck flask provided with a mercury seal, reflux condenser, and dropping funnel, add a surplus of lithium hydride- ^3H (23.5 g), and stir for a short time. (It is desirable to conduct the reaction in an atmosphere of dry air containing no CO_2 .)

Add 200 ml more of diethyl ether to the mixture and begin to introduce a solution containing 71.2 g of AlCl_3 in 300 ml of diethyl ether at a rate such that uniform boiling of the ether is observed. During this entire time stir the solution and continue the stirring a certain time after the visible termination of the reaction.

Filter off the precipitated lithium chloride and the surplus of lithium hydride in a nitrogen atmosphere. Recover the lithium aluminium hydride from the solution by distilling off the ether. Determine the yield of the lithium aluminium hydride. (When the solution is held for a longer time before filtration, the yield of the product grows and its purity improves.) Determine the specific activity of the lithium aluminium hydride with the aid of the 2π flow-type counter with a known counting efficiency, and evaluate its radiochemical yield.

Experiment 16.7. SYNTHESIS OF PROPANOL-2- ^3H VIA LITHIUM ALUMINIUM HYDRIDE [1]



Equipment and Reagents

Equipment and Utensils. A gas chromatograph and a counting installation with a flow-type counter (see Experiment 3.5, Vol. 1). A vacuum installation. A long-neck flask for 50 ml with a magnet sealed in the glass. An analytical balance.

Radioactive Substances. LiAl^3H_4 with a specific activity of 37 kBq/g (1 $\mu\text{Ci/g}$).

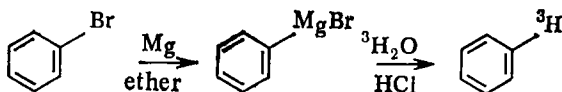
Reagents. Absolute diethyl ether. Absolute acetone. Drierite. Nitrogen (liquid). Ice.

Performance of Work

Put 0.273 g of lithium aluminium hydride- ^3H into the 50-ml long-neck flask having a magnet sealed in the glass. Connect the flask to the vacuum installation, distil 20 ml

of dry ether into it, and stir the mixture during one hour. Cool the flask with liquid nitrogen, evacuate it, and then introduce 3 ml of dry acetone into it. Hold the mixture during 30 min at -20°C , and then mix it at room temperature during one hour. Remove the ether and surplus acetone in a vacuum, and distil 1.1 ml of water to the residue. Hold the mixture for two hours at room temperature, and distil off the volatile compounds into a flask containing 15 g of Drierite. Dry the flask, put it in a mixture of ice and water (0°C), and distil the product in a vacuum. Determine the yield of propanol-2- ^3H calculated for LiAlH_4 . Find the specific activity and the yield calculated for the activity of tritium with the aid of the gas chromatograph (see Experiment 16.17).

Experiment 16.8. SYNTHESIS OF BENZENE- ^3H [1]



Equipment and Reagents

Equipment and Utensils. A gas chromatograph and a counting installation with a flow-type counter (see Experiment 3.5). An apparatus for the synthesis of Grignard's reagent. A rectification column.

Radioactive Substances. Water- ^3H with a total activity of 74 MBq (2 mCi).

Reagents. Bromobenzene. Magnesium shavings. Absolute diethyl ether. Na_2CO_3 . CaCl_2 . Na (metallic). Solutions: 60% HClO_4 , concentrated HCl .

Performance of Work

(a) Phenyl Magnesium Bromide

Put 7.2 g of magnesium shavings preliminarily dried in a drying cupboard at 120°C during 10-15 min into a 500-ml three-neck flask provided with a mechanical stirrer, a reflux condenser, and a dropping funnel. Protect the condenser and the dropping funnel with calcium chloride tubes, after which pour in 200 ml of absolute diethyl ether to the magne-

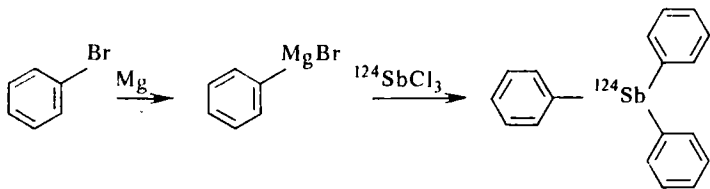
sium shavings. Put a solution of 31.2 ml of freshly prepared bromobenzene in 154 ml of absolute ether into the dropping funnel, switch on the stirrer and introduce 10-15 ml of this solution into the flask. Should the reaction fail to begin in a few minutes (slight boiling of the ether), heat the flask a little on a water bath. Should the reaction again fail to begin, add several minute crystals of elementary iodine (0.1-0.2 g) to the reaction mixture. Determine the beginning of the reaction according to the vanishing of the colour and the appearance of turbidity in the solution. Next introduce the bromobenzene solution into the reaction flask so that constant boiling of the ether is maintained. After adding the entire ether solution of bromobenzene, heat the reaction mixture on a water bath for one hour. Upon completion of the reaction, transfer the ether solution of Grignard's reagent into a flask with a ground-glass stopper and store it in a dark place.

(b) Benzene-³H

Pour the filtered off ether solution of Grignard's reagent into another portion of dry ether containing a mixture of water-³H and HCl in an amount somewhat less than the equivalent one. Add the Grignard solution rapidly with vigorous stirring (a reflux condenser and external cooling are needed). After the entire water-³H has reacted, bring the decomposition of the reagent to the end by adding hydrochloric acid. Wash the ether solution with water, a soda solution, and again with water. Dry over calcium chloride, and distil in a column. Terminate the distillation when the temperature of the distillate reaches 35 °C, after which remove the remaining ether by extraction with two portions of 60% perchloric acid (it does not lead to hydrogen exchange). If it is hard to separate the two layers completely, shake the aqueous layer with a certain amount of unlabelled benzene, which is then combined with the main fraction.

Wash the organic layer with water, a soda solution, again with water, and dry it over calcium chloride. Distil the benzene twice at atmospheric pressure over sodium in a small column and determine the yield. Determine the specific activity and the yield according to the activity with the aid of a gas chromatograph (see Experiment 16.17).

Experiment 16.9. SYNTHESIS OF TRIPHENYLSTIBINE- ^{124}Sb [4]



Equipment and Reagents

Equipment and Utensils. A counter with a detector of γ -radiation. An arrangement for synthesis (Fig. 16.1). A distilling apparatus. A sectional funnel for filtration. An analytical balance. A beaker for 1.5 litres. A separatory funnel for 0.5 litre. Beakers for 100 ml (2). A crystallizer. A Büchner filter.

Radioactive Substances. An ether solution of SbCl_3 containing ^{124}Sb with a total activity of $\sim 1.5 \times 10^5$ cpm.

Reagents. SbCl_3 . Absolute diethyl ether. Magnesium (shavings). Bromobenzene (dry). Iodine (crystalline).

Performance of Work

(a) Antimony Trichloride- ^{124}Sb

Put a weighed sample (40-60 g) of commercial antimony trichloride into the flask of the distilling apparatus, and add the initial active solution with $^{124}\text{SbCl}_3$ in an amount such that the mass specific activity of the product would be ~ 5000 cpm/mg. Check the tightness of the distilling apparatus beforehand. Distil the antimony trichloride into the receiver, collecting the fraction boiling at $221 \pm 1^\circ\text{C}$.

Take a weighed amount (0.2 g) of the distilled product after cooling and thorough trituration in a porcelain mortar, and dissolve it in a known volume of ethanol, let aliquot volumes of the solution stand for evaporation in measuring bowls. According to the measured activity of the samples, determine the mass specific activity of the prepared labelled antimony trichloride.

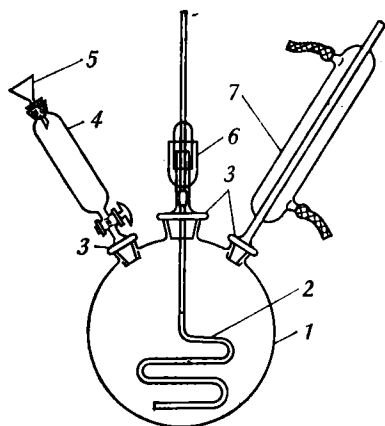


Fig. 16.1. Arrangement for synthesis of triphenylstibine:
 1—three-neck flask; 2—stirrer; 3—ground-glass joints;
 4—separatory funnel; 5—conical funnel; 6—glycerin seal;
 7—reflux condenser

(b) *Triphenylstibine*- ^{124}Sb

Put 10 g of magnesium shavings, 50 ml of absolute ether, and 25 ml of an ether solution of bromobenzene (65 g of anhydrous bromobenzene in 200 ml of anhydrous ether) into the reaction flask of the arrangement for synthesis (Fig. 16.1). To initiate the reaction, introduce a few minute crystals of iodine into the flask and heat the mixture slightly on a water bath. After the reaction begins, stop the heating, add another 50 ml of the anhydrous ether to the flask and gradually pour in the remaining amount of the bromobenzene ether solution at a rate such that the mixture will boil weakly (1-1.5 h). To prevent the reaction from proceeding too violently, cool the flask containing the reaction mixture with a mixture of ice and salt.

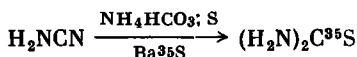
After completing the addition of the bromobenzene, slowly add to the reaction mixture through a funnel a previously prepared solution containing 28.5 g of $^{124}\text{SbCl}_3$ in 75 ml of absolute ether (the duration of this operation is about one hour). When the $^{124}\text{SbCl}_3$ has been added, boil the mixture another 30 min on a water bath. Next cool the reaction mixture and slowly pour it out while stirring into a vessel containing one litre of pure water with ice. Thoroughly

stir the mixture, and then pass it through the Büchner filter, extract the residue on the filter three times with ether (in 30-ml portions). Separate the aqueous layer and also extract it twice with ether (in 60-ml portions). Carefully evaporate the combined ether extracts on a water bath in a porcelain bowl, add molten CaCl_2 , and let it stand overnight.

To remove the diphenylstibine contaminant, dissolve the "dry" product obtained with heating in 70 ml of petroleum ether, filter it while hot through a paper filter, and let it crystallize. The triphenylstibine separates upon cooling and evaporation of the solvent in the form of small prisms.

Dry the triphenylstibine crystals in the air, determine their melting point and compare it with the data given in a reference book. Determine the total amount of the labelled triphenylstibine obtained and its specific activity. Calculate the yield of triphenylstibine.

Experiment 16.10. SYNTHESIS OF THIO- ^{35}S -UREA [4]



Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. An apparatus for distillation with steam. An apparatus for evaporation in a vacuum. An analytical balance. A jar for 25-30 ml with a ground-glass stopper. A long-neck flask with a cooler. A foam trap. A vacuum desiccator. A funnel for filtration.

Radioactive Substances. BaS containing ^{35}S with a specific activity of 0.4 MBq/g ($\sim 10 \mu\text{Ci/g}$).

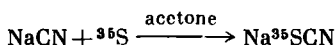
Reagents. H_2NCN . NH_4HCO_3 . Sulphur.

Performance of Work

Put 0.36 g of pure cyanamide, 1.2 g of ammonium bicarbonate, less than 0.5 g (traces) of finely ground sulphur, 1.3 g of barium sulphide- ^{35}S and 15 ml of water into a jar with a ground-glass stopper. Shake the mixture at 25-30 °C during three hours, then transfer it into the long-neck flask and during one hour heat it up to 60 °C, after which boil it. Connect the foam trap and the cooler to the flask and pass steam through it. Distil off 30-40 ml of water up to a negative

alkaline reaction of the distillate. Filter off the hot mixture, wash the precipitate with a small amount of hot water, and evaporate the filtrate at a reduced pressure to a volume of 2-3 ml. Dry the residue in the vacuum desiccator. Determine the melting point, specific activity of the thiourea, and its yield.

Experiment 16.11. SYNTHESIS OF SODIUM THIOCYANIDE- ^{35}S [1]



Equipment and Reagents

Equipment and Utensils. A counting installation with a detector of β -radiation or an end-window counter. An analytical balance. A pear-shaped flask for 10 ml. A cooler. A gasometer.

Radioactive Substances. Elementary sulphur containing ^{35}S with a specific activity of 37 kBq/g (1 $\mu\text{Ci/g}$).

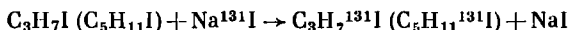
Reagents. Acetone. NaCN. Concentrated H_2SO_4 . Nitrogen (in a cylinder).

Performance of Work

Heat a mixture containing 0.056 g of sodium cyanide (*be careful—it is poisonous!*), 0.04 g of ^{35}S , and 1.7 ml of acetone with a reflux condenser during 45 min. Combine the acetone solutions and evaporate in a stream of nitrogen and dry the residue over concentrated sulphuric acid.

The yield of the reaction product is quantitative. The product contains a small amount of sulphur that can be removed by extraction with water and centrifuging. After purification and drying over sulphuric acid, determine the specific activity of the product.

Experiment 16.12. PREPARATION OF PROPYL IODIDE- ^{131}I (OR ISOAMYL IODIDE- ^{131}I) [5]



Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. A small motor with a stirrer. A flask for 25-30 ml. A cooler. A dephlegmator. A sectional funnel for filtration. A pipette with a syringe. A separatory funnel for 10-15 ml.

Radioactive Substances. A solution of NaI containing ^{131}I with a specific activity of 5×10^3 cpm/ml.

Reagents. Propyl iodide (or $\text{C}_5\text{H}_{11}\text{I}$). Diethyl ether. CaCl_2 .

Performance of Work

Introduce 1 ml of $\text{C}_3\text{H}_7\text{I}$ (or 1.3 ml of $\text{C}_5\text{H}_{11}\text{I}$) and 10 ml of a 1 *M* solution of Na^{131}I into a flask provided with a stirrer and a reflux condenser. Switch on the stirrer and begin to heat the flask on a water bath. Stop the heating in 15-20 min after the beginning of boiling of the water bath. Extract the propyl iodide- ^{131}I (isoamyl iodide) three times with ether in 10-ml portions.

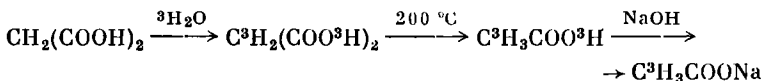
Combine the ether extracts, dry them over roasted CaCl_2 , and distil off the ether (through the dephlegmator without fail) on a water bath (40°C). If necessary, redistil in a vacuum. Use the pipette to put 0.5 ml of the dried and distilled propyl iodide- ^{131}I into the 10-15-ml separatory funnel. Introduce 5 ml of water into the funnel. Shake the mixture and separate the layers. Precipitate silver iodide- ^{131}I from the aqueous layer. Separate the precipitate in the sectional funnel for filtration, dry the preparation, and prepare it for activity measurement.

Determine the specific activity of the propyl iodide- ^{131}I (isoamyl iodide) and calculate the degree of isotope exchange.

Experiment 16.13. SYNTHESIS

OF ACETIC- ^3H ACID [6]

Acetic acid labelled in the methyl group can be prepared by decarboxylation of malonic acid that is preliminarily labelled by dissolving in tritium water:



Equipment and Reagents

Equipment and Utensils. A counting installation with a 2π flow-type counter (SOT-25-BFL). An arrangement for synthesis (Fig. 16.2). A vacuum pump. A burette.

Radioactive Substances. Tritium water with a specific activity of 74 kBq/ml ($2 \mu\text{Ci/ml}$).

Reagents. Malonic acid. Chloroform. Nitrogen (liquid). Phenolphthalein. A 2 *N* solution of NaOH.

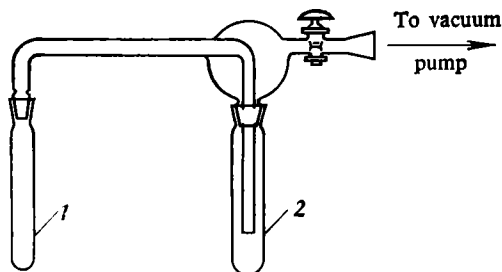


Fig. 16.2. Arrangement for the synthesis of acetic- ^3H acid:
1—reaction test tube; 2—receiver

Performance of Work

Put 0.3 ml of malonic acid and 0.5 ml of tritium water into test tube 1 (Fig. 16.2) and let it stand overnight in the closed arrangement. Cool receiver (test tube) 2 with liquid nitrogen, evacuate the air from the arrangement, and freeze out the surplus water in receiver 2. Change receiver 2, again evacuate the air from the arrangement, and cool receiver 2 with liquid nitrogen. Carefully heat the labelled malonic acid in test tube 1 up to 200°C , as a result of which it is decarboxylated. Freeze out the formed acetic- ^3H acid in test tube 2.

Upon completion of the reaction, raise the temperature of the trap to about -75°C by changing the cooling mixture (chloroform with liquid nitrogen) and remove the CO_2 with the aid of the vacuum pump. Acetic- ^3H acid remains in receiver 2. Transfer it into the sodium salt by titration with a 2 *N* solution of NaOH in the presence of phenolphthalein.

Evaporate the solution and determine the activity of the dry $\text{C}_3\text{H}_3\text{COONa}$ by means of the 2π flow-type counter.

Experiment 16.14. PHOTOSYNTHESIS OF SUGARS [7]

Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window counter. An arrangement for photosynthesis (Fig. 16.3). A Soxhlet apparatus. A centrifuge. Chromatographic columns. A daylight

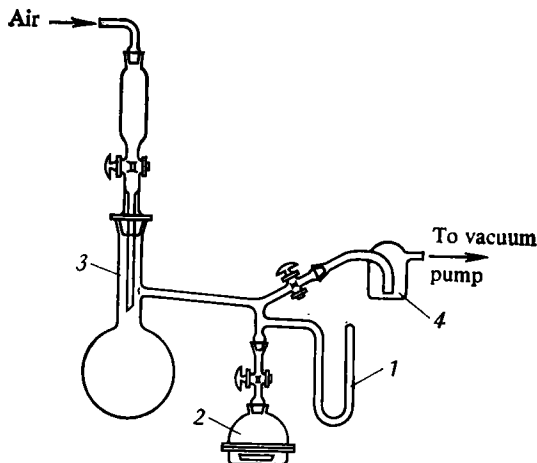


Fig. 16.3. Arrangement for the photosynthesis of sugars:
1—manometer; 2—vacuum-desiccator; 3—flask for producing $^{14}\text{CO}_2$; 4—bubbler with baryta water

lamp. Petri dishes. A funnel for filtration. A burette. Flasks for 5-10 ml. A chromatographic cylinder. A gasometer.

Radioactive Substances. BaCO_3 containing ^{14}C with a specific activity of 18 MBq/g (~ 0.5 mCi/g).

Reagents. Glucose. Absolute acetone. Ethanol (96%). Bromophenol blue. Activated carbon. A cation and anion exchangers. Chromatographic paper. Nitrogen (in a cylinder). AgNO_3 . Solutions: concentrated and 10% H_2SO_4 , 5 M NH_4OH ; 10% $(\text{CH}_3\text{COO})_2\text{Pb}$. Baryta water.

Performance of Work

Put a vegetative material in the form of disks prepared from leaves of flower-garden tobacco (3-4 months old) in a flat bowl on the surface of water with their stoma upward. Transfer the bowl into the vacuum-desiccator connected to a water-jet pump, a mercury manometer and a flask for producing $^{14}\text{CO}_2$ (Fig. 16.3). Introduce $\text{Ba}^{14}\text{CO}_3$ into the flask, close the latter with a stopper having a dropping funnel containing concentrated sulphuric acid. Evacuate the air from the system to a pressure of $(1.3-2.0) \times 10^4$ Pa and then disconnect it from the water-jet pump.

By letting sulphuric acid drop onto the $\text{Ba}^{14}\text{CO}_3$, fill the vacuum-desiccator with $^{14}\text{CO}_2$. Scavenge the device for producing $^{14}\text{CO}_2$ with air and switch it off when the pressure

almost reaches atmospheric (9.8×10^4 Pa). Separate the vacuum-desiccator from the manometer and leave it under the daylight lamp to the following day.

Next, alternately evacuating the gas from the desiccator and admitting nitrogen, free the desiccator of gaseous $^{14}\text{CO}_2$. Monitor the completeness of removal of the CO_2 by passing the nitrogen from the desiccator through bubbler 4 filled with baryta water. Extract the vegetative disks and "fix" them by boiling for five minutes in 96% ethanol.

Transfer the disks into the Soxhlet apparatus and extract with 80% ethanol for two hours (up to complete decolourization of the disks). Evaporate the alcohol solution in a vacuum until dry, transfer the precipitate onto the filter and wash it several times with small portions of water. Introduce a small amount of 1% sulphuric acid into the filtrate and hydrolyze on a boiling water bath with stirring during 30 min (the sugars decompose into hexoses). Neutralize the acid solution with a hot solution of NaOH (according to bromophenol blue the pH is 3.0-4.6) with stirring. Terminate the neutralization when the yellow colour vanishes. Separate the precipitate by centrifuging, wash it two or three times with small portions of distilled water and discard it. Add a 10% solution of lead acetate from a burette to the solution (100-150 ml) up to complete precipitation of the proteins. Heat and filter the solution. Add 0.5 g of activated carbon to the filtrate, and boil the solution with constant stirring for 10-15 min. Filter off the carbon, wash it with distilled water, and discard it. Evaporate the filtrate to 30-50 ml and pass it through columns with a cation exchanger (10 g) and an anion exchanger (10 g) at a rate of 2 ml/min.

Wash off the active precipitate with distilled water. Evaporate the solution (it must have a neutral reaction) in a vacuum up to 50 ml, purify it again with activated carbon, and evaporate until dry in a vacuum in a preliminarily weighed flask. For final purification, perform crystallization on a carrier. For this purpose, put about 200 mg of chemically pure glucose and 0.5 ml of water into a flask and after dissolving of the precipitate add 3 ml of 96% ethanol. Next while stirring add anhydrous acetone dropwise up to stable turbidity. Close the flask and place it for two days in a refrigerator. Filter off the precipitate, dry it in the air, place it in a glove box, and measure its specific activity.

Check the purity of the separated product by the method

of paper chromatography. For this purpose, use a micropipette to apply 0.01-0.02 ml of a 0.5-1 % solution of the separated glucose in 50-80 % ethanol onto a sheet of chromatographic paper 25×400 mm in size at a distance of 30 mm from its lower end. The size of the spot must not exceed 1 cm in diameter. Dry the spot with warm air and place the chromatogram into a sealed glass cylinder with a solvent (*n*-butanol-acetic acid-water in the ratio 4 : 1 : 5, take the upper saturated layer).

Perform the chromatographing during 18-20 h, after which extract the chromatogram from the cylinder, dry it, spray an ammonia solution of silver nitrate (mix an 0.1 *M* solution of AgNO_3 with 5 *M* aqueous ammonia in the ratio 1 : 1) over it and dry slightly in a drying cupboard. The compounds reducing the ammonia solution of silver nitrate are developed in the form of brown spots on a weakly brown background. The ratio of the speeds of travelling of the glucose and of the solvent front is 0.50.

Experiment 16.15. SYNTHESIS OF PROLINE- ^3H [8]

It is not always possible to introduce tritium into organic compounds by a conventional synthetic method or by isotope exchange. The former is hardly acceptable because of its involved and cumbersome nature and is inevitably associated with large losses of the isotope in the course of synthesis, while the isotope exchange of hydrogen can be achieved for far from all types of compounds. This is why it is often good practice to introduce tritium into complex organic substances by using reactions of recoil atoms. Lithium compounds are a source of recoil atoms of ^3H . The reaction of the formation of a tritium recoil atom $^3\text{Li}(n, \alpha)^3\text{H}$ has a cross section of $9.45 \times 10^{-26} \text{ m}^2$ (945 barn), and notwithstanding the small content of ^6Li in the isotope mixture (7.5 %), the tritium yield is sufficiently high. By irradiating 1 g of natural lithium with a flux of slow neutrons ($1 \times 10^{12} \text{ cps/cm}^2$) during one hour, one can obtain a preparation having a specific activity of 37 MBq/g·h [1 mCi(g·h)].

Equipment and Reagents

Equipment and Utensils. A nuclear reactor with a neutron flux of $6 \times 10^{12} \text{ cps/cm}^2$. A vacuum pump. A α counting installation with a 2π flow-type counter (SOT-25-BFL). A glove box for working

with β -radioactive substances. An analytical balance. An airtight cylinder. Beakers. Quartz ampoules. An aluminium container.

Reagents. Proline. Reinecke salt— $\text{NH}_4[\text{Cr}(\text{NH}_3)_2(\text{SCN})_4] \cdot \text{H}_2\text{O}$. Absolute diethyl ether. Absolute ethanol. Li_2CO_3 .

Performance of Work

Put 1 g each of proline and lithium carbonate into a quartz ampoule with a volume of about 35 cm^3 . Evacuate the air from the ampoule to a pressure of 1.33 Pa, seal it, place it in the aluminium container, and irradiate it in the nuclear reactor during 15 h. Next heat the ampoule for several hours at 100°C in a drying cupboard, and after cooling, open it in the glove box. Treat the contents of the ampoule several times with small portions of absolute diethyl ether for separating pyrrolidine and pyrrole. Combine the extracts and concentrate them to a small volume at a temperature not over 40°C . The method of gas chromatography can be used to determine the amount of amines and their specific activity.

Dissolve the residue after extraction, which contains proline, in absolute ethanol, and filter the solution to remove lithium carbonate. Check for the absence of impurities by paper chromatography.

Evaporate the alcohol solution of proline on a water bath until dry, and dissolve the residue in a small volume of water. To the acid (according to congo-red test paper) solution at 60°C add Reinecke salt in an amount corresponding to 9 g per 100 ml of water. Precipitate slowly. Filter off the evolved salt (the product of combining with proline), dry and weigh it. Use the flow-type counter to measure the specific activity of the preparation and determine the yield of the proline.

Experiment 16.16. SYNTHESIS OF ANTIMONY TRIBROMIDE- ^{82}Br [9]

Equipment and Reagents

Equipment and Utensils. A counter with a detector of γ -radiation. An arrangement for synthesis (Fig. 16.4). A Kipp gas generator. An analytical balance. A measuring flask for 100 ml. A sectional funnel for filtration. A Büchner filter. Traps with desiccants.

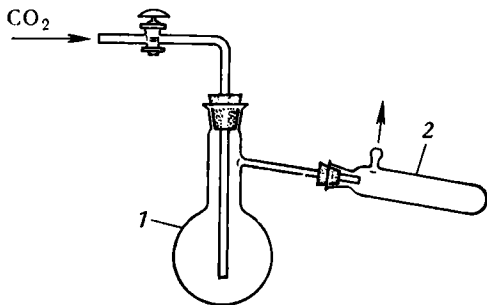


Fig. 16.4. Arrangement for synthesis of antimony tribromide:
1—reaction flask; 2—receiver

Radioactive Substances. A solution of NaBr (0.1 *M*) containing ^{82}Br with a specific activity of 3×10^4 cpm/ml.

Reagents. SbBr_3 . Solutions: 0.5 *N* HNO_3 ; 0.5 *M* AgNO_3 .

Performance of Work

Pour 1 ml of a sodium bromide solution containing ^{82}Br into a small Wurtz flask and evaporate it until dry. Assemble an arrangement for synthesis (Fig. 16.4) and fill it with dry CO_2 . Carefully add 0.5 g of antimony tribromide (*it hydrolyzes in the air!*) to the contents of reaction flask 1. Close the flask with a stopper, immerse it into boiling water, and heat it during 3-6 h.

Distil off the formed antimony tribromide- ^{82}Br into receiver 2 by heating the flask with the flame of a burner. Carefully hydrolyze the distillate in the test tube with water, transfer the mixture into the 100-ml measuring flask and dilute with water, bringing the volume up to the mark. Take two 10-ml samples, acidify them with 0.5 *N* nitric acid, boil and precipitate silver bromide by adding a 0.05 *M* solution of silver nitrate. Separate the precipitate in the Büchner filter and prepare specimens for measuring the activity of the preparations in the counter.

Take two samples (0.1 ml each) of the initial sodium bromide solution containing ^{82}Br and precipitate bromine in them in the form of silver bromide. Separate the precipitates in the Büchner filter, prepare them for measurement in the usual way, and measure their activity in the counter.

Calculate the specific activity (in cpm/ml) of the initial

sodium bromide preparation and the obtained antimony bromide. Use these data to calculate the fraction of radioactive bromine that has passed into the SbBr_3 .

Experiment 16.17. ANALYSIS OF LABELLED COMPOUNDS [10]

The fundamental characteristics in appraising the applicability of methods of synthesizing labelled compounds are the radiochemical yields of all the useful products, their radiochemical, chemical, and isotope purity, specific activity, and the specific nature of the "tracer".

The total radiochemical yield determines the fraction of an isotope that is utilized. The radiochemical yields characterize the fractions of the radioactive isotope registered in the individual components of a mixture of products formed in synthesis.

The specificity of the tracer, which is measured by the fraction of radioactive atoms in a fixed position in a molecule, must be taken into account when studying the mechanisms of chemical, biochemical, and other processes with the participation of labelled compounds.

The chemical and radiochemical purity of the substance used, which is determined by the content of both inactive and radioactive impurity molecules, is essential in all investigations with labelled compounds. A no less important parameter is the isotope purity, determined when measuring the half-lives and energy spectra of radiations.

The expediency of the practical use of labelled compounds is determined by their specific activity, whose lower limit must correspond to the thresholds of sensitivity of the activity measuring methods, while the upper one is chosen in accordance with the radiation decay of the labelled substance in storage and when used.

All the above characteristics of radioactive preparations can be found only with a properly chosen scheme of analysis of the labelled compounds. The most important operations in analysing complicated mixtures of labelled substances is their separation into components, measurement of the summary activities and activities of the components, and also determination of the fraction of radioactive atoms in the fixed positions of a molecule.

A variety of methods are used for separating mixtures, including crystallization, coprecipitation, extraction, distillation, chromatographic methods, and electrophoresis. Gas chromatography is one of the promising methods of investigating gaseous and readily volatile specimens. Gas-liquid chromatography makes it possible not only to effectively separate a mixture, but also (when using methods of complex detection) provides the possibility of rapidly determining the specific activity and radiochemical yield of the products. Such methods also make it possible to appraise the chemical and radiochemical purity of the labelled preparations.

In a number of cases when analysing substances that readily pass through a chromatographic column, gas-liquid chromatography yields results needed for appraising the summary activity of specimens. If part of the compounds in a mixture are retained on the sorbent, additional operations are needed to determine the summary activity. Particularly, the summary activity of a mixture of organic substances labelled with the isotopes ^{14}C or ^3H can be measured by the method of burning active weighed samples while using Geiger-Müller counters, the scintillation method with dissolving of a weighed sample in a liquid scintillator, etc.

To study the intramolecular distribution of the activity, the pure component must be separated from the mixture with or without a carrier and subjected to chemical analysis that will make it possible to measure the fraction of the activity due to the radioactive atoms in a definite position in a molecule. For example, to determine the fraction of ^{14}C in the carboxyl group of labelled organic acids, the reaction of decarboxylation can be performed. When studying the distribution of atoms of the isotope ^{14}C in molecules of picolines, it is comparatively simple to determine the ratio of the amounts of ^{14}C contained in the methyl group and in the ring. This is done by carrying out reactions of oxidation of the methyl group with following decarboxylation and measurement of the activity of the pyridine carboxylic acid and pyridine.

The object of the present experiment is to determine the summary activities of gaseous and liquid products labelled with ^{14}C and formed when pyridine is irradiated in a nuclear reactor. Simultaneously with separation in a gas chromato-

graph, the radiochemical yields of the components and their specific activities are measured. The intramolecular distribution of the activity in labelled picoline is studied.

Equipment and Reagents

Equipment and Utensils. A counting installation with a liquid scintillation counter. A gas-liquid chromatograph with double detection (according to the thermal conductivity and the radioactivity) having a three-way cock and traps at its outlet (see Experiment 3.5 in Vol. 1). A microsyringe. A water bath. A round-bottom flask with a reflux condenser and a stirrer. A device for distillation under a vacuum. A Büchner filter. Thermometers for 50 and 200 °C.

Radioactive Substances. Quartz ampoules with pyridine irradiated in a nuclear reactor. An ampoule with labelled pyridine or benzene with a specific activity of 5×10^4 Bq.

Reagents. α -Picoline. KMnO_4 . A dilute solution of H_2SO_4 . Helium (in a cylinder). Nitrogen (liquid).

Performance of Work

Before beginning work, acquaint yourself with the design and rules for the use of a counting installation with a liquid scintillation counter and of a gas-liquid chromatograph.

Measuring the Summary Activity of the Gaseous Fraction.

Prepare the chromatograph for analysing the gaseous fraction in the irradiated samples with pyridine. Perform the analysis at room temperature, a helium rate of flow of 20 ml/min, and a rate of flow of lighting gas (from the mains) of 40 ml/min. Put the irradiated ampoule into a device for breaking ampoules connected to the inlet of the chromatographic column. Break open the ampoule and count the activity of the gaseous fraction with the aid of a proportional counter. When the background is reached, stop the count. Extract the ampoule from the chromatograph and transfer it into a test tube with a ground-glass stopper.

Measuring the Summary Activity of the Liquid Fraction.

Prepare the counting installation with the liquid scintillation counter. Cool the ampoule with the irradiated pyridine, open it, and take a sample of 0.001 ml with the microsyringe. Transfer the sample into a small bottle containing 5 ml of the solution of the scintillator in toluene. Measure the activity of the prepared specimen and the background by the scintillation method. Calculate the specific activity of the irradiated specimen with a view to the effectiveness of measurements for the isotope ^{14}C .

Measuring the Activity of Highly Volatile Components.

Prepare the gas-liquid chromatograph for analysing the volatile components in the irradiated sample. Set the temperature of the column thermostats at 120 °C, of the detector thermostats at 170 °C; bring up the rate of flow of the carrier gas (helium) to 20 ml/min, and of the lighting gas to 40 ml/min. Raise the temperature of the evaporator in the chromatograph to 170 °C. Use the microsyringe to take samples of 0.01 ml each from the cooled ampoule with labelled pyridine or benzene. Introduce a sample into the evaporator, noting the time of introduction of the sample. Register the peak of the benzene on chromatograms with recording of the signals of the katharometer and the proportional flow-type counter. Introduce 0.015 ml of the liquid fraction from the cooled ampoule with the irradiated pyridine into the heated evaporator. Note the instant of introducing this sample and record the readings of the instruments registering the change in the thermal conductivity and activity in the gas stream. Use the readings of the proportional counter (I_i , count) for the separated peaks to calculate the activity of the corresponding mixture component:

$$A_i = (I_i - I_b) \frac{v}{V}$$

where A_i is the counting rate, cpm; I_i is the integral activity at the peak, count; I_b is the integral background during the time of passage of the peak, count; v is the total rate of flow of the helium and the lighting gas, ml/min; and V is the volume of the counter, ml.

Calculate the relative retention times and relative retention volumes for each component fixed on the chromatograms (see Chap. 3, Vol. 1). Identify the peaks by comparing the experimental data on the relative retention volumes with the data given below.

Substance . . .	Benzene	Toluene	Pyridine	α -Picoline	β -Picoline
Relative retention volume . .	1.00	2.05	2.95	4.11	6.51

Determine the radiochemical yields of the components (P_i in %):

$$P_i = 100A_i/A$$

where A_i is the activity of a component calculated for 1 ml of the mixture, cpm, and A is the summary activity of the gaseous and liquid fractions calculated for 1 ml of irradiated pyridine, cpm.

Studying the Intramolecular Distribution of ^{14}C Atoms in α -Picoline. Connect the system of traps cooled by dry ice to the outlet of the chromatograph through the three-way cock. Heat the evaporator in the chromatograph up to 170°C and with the aid of the syringe inject a sample containing 0.1 ml of inactive α -picoline and 0.2 ml of the mixture from the irradiated ampoule. Note the instant when the sample is introduced. Watch the signal of the katharometer and at the instant when the α -picoline passes through the detector collect it in the cooled trap. When the passage of the peak of the α -picoline terminates, disconnect the trap with the aid of the three-way cock. Remove the trap with the frozen out fraction and weigh the preparation. Take a 0.01 ml sample with the microsyringe and analyse it chromatographically. Transfer the remaining α -picoline into a three-neck flask provided with a stirrer and a reflux condenser, and add a calculated amount (1 : 60) of water. Put the flask on the water bath, heat it to 70°C , and introduce 0.1 of the calculated amount of KMnO_4 (1 : 3.6) seeing that the temperature in the flask does not exceed 90°C . Introduce the entire KMnO_4 in the same way in portions. After complete decolorization, cool the mixture, filter it, and wash the filter with 4 ml of hot water. Distil off the water in a vacuum up to half of the initial volume, again add water acidified with sulphuric acid (up to an acid reaction to congo-red test paper) and again distil off half of the water. Cool the mixture and filter off the precipitated crystals of pyridine carboxylic acid.

Evaporate the remaining liquid and filtrate until almost dry and after cooling filter off the precipitated crystals again. Wash the crystals of picolinic acid on the filter with several drops of cold water and dry them.

Take a weighed sample (10 mg) of crystalline pyridine carboxylic acid. Dissolve it in 5 ml of a scintillation solution. Transfer the solution into a small bottle and measure the activity of the sample in the installation with the liquid scintillation counter. Calculate the specific activity of the separated preparation, and process the data with account taken of the effectiveness of the counter for ^{14}C .

To perform decarboxylation, carefully heat the remaining crystals of the acid up to melting in the flask provided with a reflux condenser. Continue the heating until the evolution of CO_2 bubbles stops, add a carrier, 0.1 ml of pyridine, and distil off the pyridine. Take 0.01 ml of the collected substance with the syringe, and transfer it into the bottle with the scintillator solution. Measure the activity in the installation with the liquid scintillation counter. Calculate the specific activity of the pyridine. Take a new 0.01-ml sample and introduce it with the syringe into the heated evaporator of the chromatograph, analysing it as described above.

Process the chromatograms obtained in analysing the separated labelled pyridine and α -picoline. Determine the radiochemical purity from the data on the activity of the peaks of the basic substances and the impurities. Appraise the content of chemical impurities according to the area of the peaks registered by the katharometer.

Use the obtained values of the specific activities of pyridine carboxylic acid and pyridine to calculate the fraction of the ^{14}C atoms D_r fixed in the pyridine ring and D_{sg} fixed in the side group:

$$D_r = S_2/S_1 \quad D_{sg} = (S_1 - S_2)/S_1$$

where S_1 is the specific activity of the pyridine carboxylic acid, Bq/mol, and S_2 is the specific activity of the pyridine, Bq/mol.

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Chapter 17 Radioactive Isotopes in Chemical Analysis [1, 2]

In quantitative analysis, the method of direct precipitation of the element being determined by a radioactive reagent of a known concentration and specific activity is used. Titration with radioactive isotopes used as indicators is also employed. The method of isotope dilution is widely used for the quantitative analysis of complex mixtures. What is known as activation analysis has been included in the practice of analysing small amounts of impurities. Greater and greater attention is being given to the use of physical methods of analysis involving the absorption, reflection, and transformation of the radiation of radioactive isotopes directed onto an object being analysed.

To determine radioactive elements, radiochemical analysis is used, in which the amount of radioactive elements is determined by the absolute or relative method according to the radiation. Radiochemical analysis is also used to determine the content of radioactive isotopes in natural objects. The accuracy of the analyses is determined almost completely by the accuracy of measuring the activity, while the sensitivity is determined by the activity of the indicator (tracer) used.

Experiment 17.1. CHECKING THE PURITY OF SEPARATING ELEMENTS BY THE METHOD OF RADIOACTIVE TRACERS [3]

In separating chemical elements by precipitation, distillation, extraction, the chromatographic method, and the like, the purity of the preparations can be checked by the method of radioactive indicators or tracers. To a mixture of

substances being separated, their radioactive tracers are added—the same substances or elements containing a radioactive isotope. After separation of the mixture, the presence or absence of the given radioactive substance in the components of the mixture being separated is checked. If radioactive tracers of several elements have been added, the purity of separation can be determined with the aid of a spectrometer making it possible to measure the activity of each radioactive isotope separately. If it is impossible to use a spectrometer, a radioactive isotope must be introduced only into one component of the mixture, the presence of contamination by which is expected upon the separation of the other components.

The present experiment studies the separation of barium and strontium, which is a difficult analytical task. Separation is possible by precipitating barium chromate from an acetic acid solution. The method is based on the solubility of strontium chromate in acetic acid and the insolubility in it of barium chromate.

The substantial similarity of the chemical properties of barium and strontium hampers the chemical checking of the purity of separation. Such checking can be performed, however, by the method of radioactive tracers. To assay the amount of strontium in a barium chromate precipitate, their radioactive isotope ^{89}Sr is introduced into the mixture being separated as a strontium tracer.

Knowing the amount of barium and strontium in the mixture, the specific activity of the latter, the mass of the barium chromate precipitate obtained, and its activity, one can determine the degree of contamination of the barium chromate precipitate by strontium.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. A drying cupboard. A stove. A planchet. An analytical balance. A lamp for evaporation. Beakers for 150-200 ml (3). Glass bowls for measuring activity. A pipette with a syringe.

Radioactive Substances. A 1% solution of SrCl_2 or $\text{Sr}(\text{NO}_3)_2$ containing ^{89}Sr , specific activity 5000 cpm/ml.

Reagents. Solutions: 1% BaCl_2 or $\text{Ba}(\text{NO}_3)_2$; 30% (neutral) and 6% $\text{CH}_3\text{COONH}_4$; 10% $\text{K}_2\text{Cr}_2\text{O}_7$ (without SO_4^{2-}); 2 *N* HNO_3 ; 10% NH_4OH .

Performance of Work

Pour 10 ml of a 1% solution of barium nitrate or chloride with an exactly known content of barium and 10 ml of a 1% solution of a strontium salt containing ^{89}Sr into a 150-200 ml beaker. The specific activity of the strontium salt used must be known. Add 10 ml of a 30% solution of neutral $\text{CH}_3\text{COONH}_4$ to the mixture and, having heated the solution to boiling under a hood, add to it with stirring 5 ml of a 10% solution of $\text{K}_2\text{Cr}_2\text{O}_7$ containing no SO_4^{2-} ions.

After settling, pour off the cold solution from the precipitate through a paper or porous glass filter and wash the precipitate in a beaker, rinsing it with small portions of a 0.6% solution of $\text{CH}_3\text{COONH}_4$ until the rinsing water acquires a pale colour. Pour off the rinsing water from the precipitate through the same filter. Put the beaker with the precipitate under the funnel with the filter through which the rinsing water was poured off, and dissolve the precipitate, carried along by the rinsing water, on the filter with a small amount of hot 2 *N* nitric acid. Wash the filter with water. If the precipitate in the beaker did not dissolve completely during these operations, add more acid, avoiding a surplus of it.

Transfer about one-fourth of the solution into a standard bowl for evaporation and measurement of the radioactivity. Carefully evaporate the solution with the aid of the lamp under a hood, dry the residue to a constant mass in the drying cupboard at 110 °C, weigh it and measure its activity in a bowl in standard conditions.

Carefully add a dilute solution of NH_4OH to the remaining solution with stirring until the formed precipitate stops dissolving, next pour in 10 ml of a 30% solution of $\text{CH}_3\text{COONH}_4$, heat the liquid to boiling under a hood without stopping its stirring. After slow cooling, filter off the precipitate and wash it as described above.

Dissolve the precipitate in hot 2 *N* nitric acid, carefully evaporate about one-fourth of the solution under a lamp in a weighed standard bowl under a hood, dry it in the drying cupboard at 110 °C, weigh it and measure the activity of the precipitate.

Knowing the specific activity of the strontium salt used, calculate (in %) the contamination of the barium chromate precipitate with strontium chromate without reprecipitation and after purification by reprecipitation.

Next evaporate all the remaining nitric acid solution of the barium chromate under a hood, determine its mass and activity. Determine the amount of barium remaining in the solution according to the mass of the precipitate and its contamination with strontium.

Experiment 17.2. DIRECT DETERMINATION OF THE CONTENT OF CHEMICAL ELEMENTS WITH THE AID OF RADIOACTIVE REAGENTS [1, 4]

If a surplus of a precipitant labelled with a radioactive isotope is used as a precipitating reagent to determine an ion, the activity of the initial solution of the radioactive reagent and of the filtrate after precipitation can be used to determine the amount of reacted precipitant, and hence the amount of the ion being determined. Here one must know the concentration and specific activity of the radioactive reagent.

The number of equivalents of the ion being determined m_x can be evaluated by the formula

$$m_x = m_a - m_b = m_a - (I_f/S_0) \quad (17.1)$$

where m_a is the number of equivalents of the labelled reagent taken for precipitation, m_b is the number of equivalents of the labelled precipitating reagent remaining after precipitation in the filtrate, I_f is the activity of the filtrate, cpm, and S_0 is the specific activity of the radioactive reagent, cpm/equiv.

It is more convenient to measure the activity of 1 ml of solution of the precipitant and filtrate. The calculation in this case is performed as follows:

$$\begin{aligned} m_b &= m_a \frac{I'_f}{I'_0} \cdot \frac{V_0 + V}{V_0} \\ m_x &= m_a - m_b = m_a - m_a \frac{I'_f}{I'_0} \cdot \frac{V_0 + V}{V_0} \\ &= m_a \left(1 - \frac{I'_f}{I'_0} \cdot \frac{V_0 + V}{V_0} \right) \end{aligned} \quad (17.2)$$

where I'_f is the activity of 1 ml of filtrate, cpm, I'_0 is the activity of 1 ml of precipitant solution, cpm, V_0 is the volume of the precipitant solution, ml, and V is the volume of the solution being analysed, ml.

If instead of the activity of the filtrate we measure the activity of the formed precipitate, then taking into account that the number of equivalents of the ion being determined equals the number of reacted gramme-equivalents of the radioactive precipitating reagent, we have:

$$m_x = I/S_0 \quad (17.3)$$

where I is the activity of the formed precipitate.

DETERMINATION OF CATIONS WITH THE AID OF PHOSPHATE-³²P

The phosphates of metals such as Ca, Sr, Ba, Fe, Zr, and Zn are sparingly soluble compounds, and some of them are used in gravimetric analysis. Not all sparingly soluble phosphates, however, can be determined by the gravimetric method because some of them are filtered poorly, are insufficiently stable for transferring them into weight forms, etc.

The use of radioactive reagents eliminates these inconveniences. Another advantage of this method is that the precipitates do not have to be roasted. The coprecipitation of foreign salts also does not affect the results of analysis. The accuracy of analysis depends virtually completely on the accuracy of measuring the specific radioactivity and the radioactivity of the separated preparation.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. A centrifuge. A water bath. A lamp for evaporation. Pipettes for 1 ml with a syringe (2) and for 10 ml (1). A measuring flask for 25 ml. A burette for 25 ml. A beaker for 100 ml. A funnel. Glass and aluminium bowls for measuring activity.

Radioactive Substances. A 0.1 M solution (exactly) of K_2HPO_4 containing ³²P with a specific activity of 37 kBq/ml (1 μ Ci/ml).

Reagents. A solution of a salt of Ca, Ba, Sr, Fe, Zr, or Zn having a known concentration (0.1-0.3 M).

Performance of Work

Prepare a solution of $K_2H^{32}PO_4$ or $Na_2H^{32}PO_4$ with an exactly known concentration ($\sim 0.1 M$) having a specific activity of 2000-5000 cpm/ml. To determine the specific activity, transfer 1 ml of the solution into a bowl for measuring the activity, dry under the lamp, and measure the activity.

To a definite volume (V_2) of the solution being studied of an unknown concentration add a surplus of $K_2H^{32}PO_4$, which is determined according to the stopping of precipitate formation when new portions of the precipitant (volume V_1) are added. Coagulate the phosphate precipitate on the water bath, separate it by centrifuging or filtration, transfer 1 ml of the filtrate into a bowl for measuring the activity, dry it and measure its activity. Calculate the content of the cation being analysed.

Experiment 17.3. RADIOMETRIC TITRATION [5]

Radiometric titration is a member of the group of analytical methods used for the quantitative determination of ions in solutions. It can be employed if the ion being determined produces a virtually insoluble precipitate or an easily extracted compound with a reagent and if one of the reacting compounds can be labelled with a radioactive isotope. During titration, the activity of the precipitates or the solution is measured, and in extraction, that of one of the separated phases.

Three variants of this method are possible.

1. A radioactive tracer (better without an isotope carrier) is added to the solution of the element being determined, and then the drop in the activity of the solution is measured as the element being determined precipitates (is extracted).

2. Titration is performed with a reagent containing a radioactive isotope, the appearance of activity in the initial solution indicating the completeness of the reaction of precipitation (extraction) of the element being determined.

3. A radioactive tracer is added to the initial solution and the latter is titrated with a labelled reagent. The minimum activity of the initial solution corresponds to the equivalence point. It is assumed that the concentrations of the reagent and the composition of the precipitate are known exactly.

Figures 17.1 and 17.2 show curves of radiometric titration for conditions of precipitation or extraction of the element being determined. A glance at the figures reveals how the equivalence point is found graphically.

Examination of the titration curves shows that for an approximate determination of the equivalence point, it is not

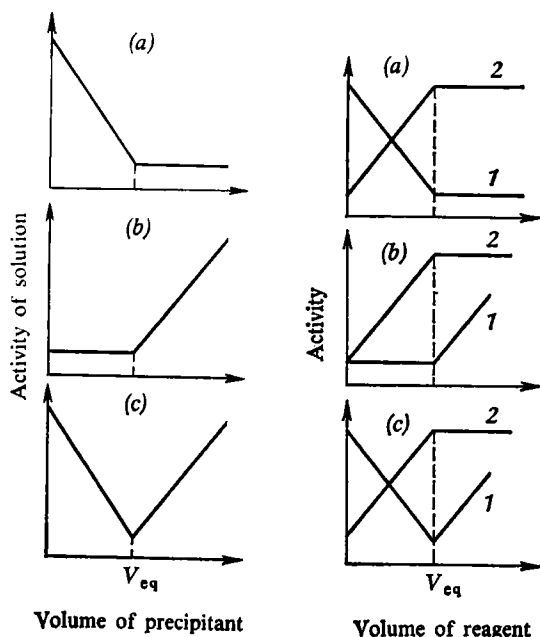


Fig. 17.1. Curves of radiometric titration by the precipitation method:
a—active solution being analysed; *b*—active reagent; *c*—active solution being analysed and reagent

Fig. 17.2. Curves of radiometric titration by the extraction method:
a—active solution being analysed; *b*—active reagent; *c*—active solution being analysed and reagent; *1*—activity of solution being analysed; *2*—activity of organic phase

necessary to obtain the entire titration curve. It is sufficient to make two (or three) measurements and then calculate the amount of precipitant corresponding to the equivalence point.

If titration is performed according to the first variant and the titration curves obtained have the form of the one shown in Fig. 17.1*a*, one should proceed as follows. Determine the initial activity I of the solution, then add the precipitant solution V_0 so that a certain activity I_f remains in the filtrate solution (it is desirable that $I_f = I/2$). The volume of the precipitant solution needed to reach the equivalence

lence point V_{eq} is evaluated by the formula

$$V_{eq} = V_0 \frac{I}{I - I_f} \quad (17.4)$$

If titration is performed according to the second variant and a curve similar to that shown in Fig. 17.1b is obtained, first it is necessary to add a surplus of the precipitant V_f' and measure the activity I_f' of the solution, and then add a second portion of the precipitant. In this case, V_{eq} is evaluated by the following formula:

$$V_{eq} = \frac{V_f' I_f'' - V_f'' I_f'}{I_f'' - I_f'} \quad (17.5)$$

where V_f'' and I_f'' are the total amount of the added solution and the activity of the solution after addition.

If titration is performed according to the third variant, a curve is obtained similar to the one shown in Fig. 17.1c. In this case, either Eq. (17.4) or (17.5) can be used for calculations depending on where the points obtained are—on the ascending or the descending branch of the titration curve.

With a small volume of the solution being titrated, a correction must be introduced into the measured activity for the change in the volume of the solution in the process of titration:

$$\Delta = \frac{V + V_0}{V} \quad (17.6)$$

where Δ is a correction factor by which the measured activity of the solution must be multiplied, V is the initial volume of the solution, and V_0 is the volume of the added solution of the precipitant.

When the compound obtained in titration is being extracted, it is possible to measure the activity of either the initial aqueous solution or of the organic phase. The volumes of the solution corresponding to the equivalence point are evaluated by the formula:

$$V_{eq} = V_0 \frac{I}{I_{org}} \quad (17.7)$$

where V_0 is the volume of the added reagent, I is the initial activity of the aqueous solution, and I_{org} is the activity of the organic phase.

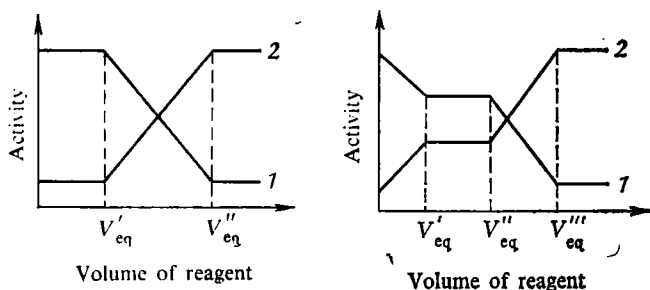


Fig. 17.3 Titration curves for a mixture of two substances being analysed using one radioactive tracer by the extraction method (the ion that is the second to enter into the reaction is labelled):
1—activity of solution being analysed; 2—activity of organic phase

Fig. 17.4 Titration curves for a mixture of three substances being analysed using two radioactive tracers by the extraction method (the ions that are the first and last to enter into the reaction are labelled):
1—activity of solution being analysed; 2—activity of organic phase; V'_{eq} , V''_{eq} , and V'''_{eq} = volumes corresponding to the equivalence points for the first, second, and third ions being determined

In radiometric titration, one radioactive tracer can be used to determine two elements present in the same solution. If, for example, we add $^{65}\text{Zn}^{2+}$ as a tracer to a solution containing ions of zinc and mercury, and then perform titration with a solution of dithizone at $\text{pH} = 4.7$, first only a complex compound of mercury forms, and a chloroform extract will be inactive. After the equivalence point for mercury (V'_{eq}) is reached, the formation of a complex compound of zinc begins that will be extracted by chloroform. The activity of the aqueous layer will begin to drop, and that of the organic phase to grow up to the equivalence point V''_{eq} for zinc (Fig. 17.3).

Using two radioactive tracers, one can determine three elements simultaneously present. In this case, the first tracer is chosen for the element forming the most stable complex compound or the most easily precipitating one, and the second one is chosen for the element forming the least stable complex compound or that precipitates only after precipitation of the first two ions. The titration curve—the depen-

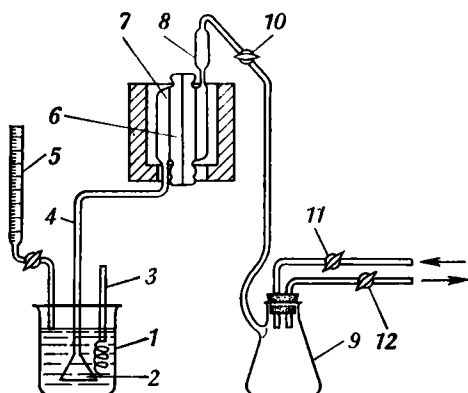


Fig. 17.5. Arrangement for radiometric titration by precipitation:
 1—vessel with solution being analysed; 2—sintered glass filter; 3—stirrer; 4—connecting tube; 5—burette; 6—counter; 7—counter jacket; 8, 9—buffer vessels; 10, 11, 12—cocks

dence of the activity of the aqueous and organic phases on the added volume of the complexing agent—has the form shown in Fig. 17.4.

Radiometric titration is performed as follows. After adding each portion of the reagent, in a certain time the activity of the solution is measured. To do this, porous sintered glass filter 2 connected to jacket 7 of liquid counter 6 (Fig. 17.5) is immersed into the solution. The jacket of the counter is connected via a three-way cock to a water-jet pump and a compressed air system. Upon connection to the water-jet pump, the transparent solution fills the jacket. After measurement of the activity, the same cock is used to connect the counter jacket to the compressed air system, and the solution is displaced completely from the jacket into vessel 1; in addition, bubbling of air through the solution results in good mixing.

Before using the arrangement for radiometric titration, one must master the procedures of working with it, and thoroughly wash it first with an acid, and then with distilled water.

In the extraction method, it is convenient to use a test tube with a ground-glass stopper as a vessel for the solution being analysed. After each portion of the reagent, the extracting agent is added to it, the phases are mixed, and the activity in one of them is determined.

A. DETERMINATION OF P

The phosphate ion is precipitated by a magnesia mixture:



This reaction can be used for the radiometric titration of either the phosphate or the magnesium ion.

Equipment and Reagents

Equipment and Utensils. An arrangement for performing radiometric titration with a detector of β -radiation (Fig. 17.5). A technical balance. A water-jet pump. A burette for 25 ml. A crystallizer. Pipettes for 5 and 1 ml with syringes. A measuring flask for 25 ml. Beakers for 100 ml (2). A measuring cylinder for 50 ml.

Radioactive Substances. A solution of Na_2HPO_4 containing ^{32}P with a volume specific activity of 18.5-37 kBq/ml (0.5-1 $\mu\text{Ci/ml}$) and a mass activity of at least 370 MBq/g (10 mCi/g) of phosphorus. A solution (0.1 M) of Na_2HPO_4 containing ^{32}P with a specific activity of $\sim 10^5$ cpm/ml.

Reagents. NH_4Cl . Solutions: concentrated NH_4OH ; 0.1 M MgCl_2 ; 0.1 M Na_2HPO_4 .

Performance of Work

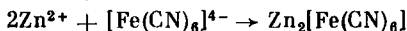
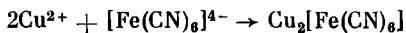
Place the solution being analysed containing an unknown amount of phosphate ion [the content of the PO_4^{3-} should be of the order of $(0.25-0.5) \times 10^{-2}$ mol] into the 25-ml measuring flask. Bring the volume of the solution up to the mark with distilled water and stir the contents of the flask. Take two 10-ml samples from the flask and put them into the 100-ml beakers. Introduce into each beaker 1 ml of a solution containing ^{32}P with a high specific mass activity, 5 ml of concentrated NH_4OH , and 5 g of solid NH_4Cl . Bring the volume of the solution up to 40-50 ml with distilled water. Place the beaker with the solution into the crystallizer with snow or ice.

Perform radiometric titration of the solution. For this purpose, add 1 ml of a 0.1 M solution of MgCl_2 from a burette into each beaker. Thoroughly mix the solution and in two or three minutes measure the activity of the solution over the precipitate. Perform the measurements with an accuracy up to 2%.

Plot the activity against the volume of the added solution and find the equivalence point. Evaluate the amount (in moles) of sodium phosphate in the specimen being analysed.

B. DETERMINATION OF Zn AND Cu WHEN BOTH ARE PRESENT

Copper and zinc form sparingly soluble precipitates with potassium ferrocyanide:



The solubility product of copper ferrocyanide is much smaller than that of zinc ferrocyanide, and for this reason, as long as copper ions are present in the solution, no zinc is precipitated by potassium ferrocyanide. Precipitation begins only after the complete precipitation of the copper ions. This is why radiometric titration of copper and zinc can be performed with potassium ferrocyanide using only a single radioactive tracer— ^{65}Zn .

As long as the copper ions precipitate, the activity of the solution containing ^{65}Zn will remain virtually unchanged and will begin to decrease when precipitation of zinc ferrocyanide starts.

The precipitates of copper and zinc ferrocyanide settle poorly, and in radiometric titration they have to be separated by centrifuging.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of γ -radiation. A centrifuge for 3-5 thousand rpm with 8 test tubes for 10 ml. A lamp for evaporation. A microburette for 1-2 ml. Pipettes for 10 and 1 ml with syringes. A measuring flask for 100 ml.

Radioactive Substances. A solution containing ^{65}Zn with a volume specific activity of 10^5 cpm/ml and a mass activity of at least 370 MBq/g (10 mCi/g).

Reagents. Solutions: 0.2 M $\text{K}_4[\text{Fe}(\text{CN})_6]$; concentrated HCl.

Performance of Work

Put the solution being analysed containing an unknown amount of copper and zinc compounds [the content of each in a sample should be $(1-3) \times 10^{-3}$ mol] into the 100-ml measuring flask. Add to it 2-3 ml of concentrated hydrochloric acid, 1-2 ml of a solution containing ^{65}Zn , and bring the volume of the mixture up to the mark. Carefully stir the content of the flask.

Put a 5-ml sample of the solution into each of eight centrifuge tubes, add 0.15 ml of a 0.2 *M* solution of $K_4[Fe(CN)_6]$ dropwise [upon the slow addition of the $K_4[Fe(CN)_6]$ no zinc is captured by the $Cu_2[Fe(CN)_6]$ to the first tube, 0.30 ml to the second tube, 0.45 ml to the third tube, and so on up to 1.2 ml to the eighth tube. Separate the precipitate by centrifuging (the speed of the centrifuge must be 3000-4000 rpm).

Take 1 ml of the transparent solution from each tube with a pipette (begin to do this from the eighth tube). In addition, take 1 ml from the measuring flask. Put each sample into a standard glass bowl for measuring the activity. Carefully evaporate the solutions until dry under the lamp and measure the activity of the obtained preparations in the counter with the detector of γ -radiation. Depict the results of the measurements graphically and determine the equivalence point. Evaluate the amount of copper and zinc in the solution being analysed.

Experiment 17.4. ANALYSIS BY THE METHOD OF ISOTOPE DILUTION [4, 6]

Analysis by the method of isotope dilution is a universal quantitative analysis with the aid of radioactive and stable isotopes. It is used for the quantitative analysis of mixtures difficult to separate because of the closeness of the physical and chemical properties of the components, for example for analysing a mixture of rare-earth elements or amino acids for which the complete separation of the components or the quantitative separation of one of them is difficult to perform, and only the partial separation of the pure components is possible. In many cases, the requirements which the conditions of quantitative separation of a component from a mixture and its purity must meet contradict each other. The method of isotope dilution makes it possible to find the quantitative composition of a mixture without resorting to the complete separation of each of the components, but only to the separation of a part of it in the pure state. The method can also be used successfully for determining small amounts of impurities that cannot be separated without losses in the process of analysis, for example, as a result of adsorption on the walls of vessels.

If a mixture contains the substance X, the amount m_X of which is to be determined, m_0 of the same substance with a different, but known isotope composition is added to the mixture. When radioactive isotopes are used, the activity I_0 of the substance being added must be known. After uniform distribution of the radioactive substance in the system (it is important here that the radioactive isotope as a result of the possible isotope exchange pass over into the composition of only a definite substance), a certain part m_1 of the pure substance X is recovered by any method, and the activity I_1 is measured. The specific activity of the recovered compound $S_1 = I_1/m_1$ equals the specific activity of the mixture after the addition of a radioactive substance to it (when an exchanging form is added, the equality of the specific activities is a result of the thermodynamic identity of the isotopes)

$$S_1 = I_0/(m_X + m_0)$$

Hence,

$$m_X = \frac{I_0}{I_1} m_1 - m_0 \quad (17.8)$$

or

$$m_X = \frac{I_0}{S_1} - m_0$$

Since $I_0/m_0 = S_0$ is the specific activity of the added radioactive substance, we have

$$m_X = m_0 \left(\frac{S_0}{S_1} - 1 \right) \quad (17.9)$$

If the added radioactive substance contains no carrier or has a very high specific activity, then $m_0 \ll m_1$, and m_0 may be disregarded in formula (17.8), whence

$$m_X = \frac{I_0}{I_1} m_1 \quad (17.10)$$

To determine the content of a radioactive substance, what is called **inverse isotope dilution** is used. It consists in adding to a mixture containing the radioactive component of interest a known amount m_0 of the same substance, but containing no radioactive isotope. After the separation of m_1 of the pure component and measuring its activity I_1 , one can use formulas (17.8) and (17.9) to calculate the amount of the radioactive substance if its total or specific activi-

ty is known. If the initial amount m_0 of the substance may be disregarded, it is easy to find the total activity of the given component by formula (17.10).

When the mixture being analysed already contains a certain amount of the labelled component and its activity is I_a , while its specific activity $S_a = I_a/m_x$, then after introducing a new portion of the initial labelled substance, as a result of dilution, the specific activity becomes equal to $(I_0 + I_a)/(m_0 + m_x)$. After the recovery of m_1 of the component with the activity I_1 , we obtain

$$\frac{I_0 + I_a}{m_0 + m_x} = \frac{I_1}{m_1} = S_1$$

or

$$m_x = \frac{I_0 - I_a}{S_1} - m_0 \quad (17.11)$$

Since

$$S_0 = I_0/m_0$$

from (17.11) we obtain

$$m_x = m_0 \frac{S_0 - S_1}{S_1 - S_a} \quad (17.12)$$

To determine m_x here, in addition to the specific activity and amount of added substance, it is also necessary to know the specific activity of the solution being studied.

The error in determination of a substance by the method of isotope dilution depends greatly on the difference between the specific activities of the radioactive substance being added and the recovered sample:

$$\frac{\Delta m_x}{m_x} 100 = \frac{S_0}{S_0 - S_1} \left(\frac{\Delta S_0}{S_0} + \frac{\Delta S_1}{S_1} \right) \quad (17.13)$$

where $\Delta m_x/m_x$ is the relative error of measurement, %, $\Delta S_0/S_0$ and $\Delta S_1/S_1$ are the relative errors in measuring the specific activity of the added and recovered substances.

The compound containing the radioactive isotope can be separated in different ways: by sublimation, precipitation, electrolysis, extraction—in other words, in any way that allows one to obtain a certain part of the compound in the chemically pure state. The amount of the separated fraction can be determined by the gravimetric method, by titration, ca-

lorimetric measurement, etc., or by calculations based on the volume and concentration of the added precipitant.

The method of isotope dilution expands the possibilities of analytical methods, but does not change their sensitivity. In the most favourable cases, the sensitivity of the method of isotope dilution equals the sensitivity of the method used to recover a part of the substance being analysed.

A. QUANTITATIVE DETERMINATION OF I⁻ IN THE PRESENCE OF Br⁻

The quantitative determination of the ions I⁻, Br⁻, and Cl⁻ when present together is a difficult analytical problem. The solubility of silver iodide, bromide, and chloride in water is low and is 1.2×10^{-8} , 8.8×10^{-7} , and 1.3×10^{-5} mol/litre. In an ammonia solution, on the other hand, silver bromide dissolves well, whereas silver iodide has a low solubility so that upon the partial separation of silver iodide from an ammonia solution a precipitate can be obtained that contains no bromide.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. An electric stove. A lamp for evaporation. A pipette for 1 ml with a syringe. Burettes for 10 ml (2). Beakers for 100 ml (3). A wash bottle with a rubber bulb. A sectional funnel for preparing precipitates for measurement. A measuring flask for 50 ml. †

Radioactive Substances. A solution of carrier-free NaI containing ^{131}I with a specific activity of 5000-10 000 cpm/ml.

Reagents. Ethanol or acetone. NaBr, NH_4NO_3 , Na_2SO_3 . Solutions: 0.05 M NaI, 0.05 M AgNO_3 , 0.01 N HNO_3 , concentrated NH_4OH , 2% transparent thermoplastic (Plexiglas) in dichloroethane.

Performance of Work

First approximately determine the activity of the initial solution of NaI containing radioactive ^{131}I . Apply 0.05-0.1 ml of the radioactive solution onto the filter of the funnel for preparing precipitates (see Vol. 1, p. 63) and measure its activity. Calculate the volume of the active solution of Na^{131}I that must be taken for the total activity to be about 5000 cpm.

Next determine exactly the activity of the initial solution. For this purpose, pour 6 ml of a 0.05 *M* solution of inactive NaI from a burette into a 100-ml beaker and add to it a volume of the radioactive solution of Na¹³¹I such that the total registered activity would be about 5000 cpm. Add 10 ml of distilled water and 2 ml of concentrated NH₄OH to the solution. Pour in 4 ml of a 0.05 *M* solution of AgNO₃ from a burette dropwise with constant stirring. For better coagulation of the precipitate, add a few minute crystals of NH₄NO₃ and carefully heat the beaker with the precipitate almost to boiling (to prevent the evolution of free iodine, it is good practice to add a few minute crystals of Na₂SO₃ to the solution). Filter the coagulated flaky precipitate in the funnel for preparing precipitates for measuring the activity through a dense filter. See that the filtrate is transparent. Wash the beaker two or three times with cold dilute 0.01 *N* nitric acid, passing the washing water through the filter, and remove the precipitate remaining on the walls with a piece of filter. Next wash the precipitate with small portions of distilled water and ethanol or acetone. Let the precipitate dry in the funnel with the water-jet pump open (to prevent decomposition of the precipitate under the action of light, cover the funnel with the lid from a crucible). Measure the activity of the precipitate with an accuracy up to 3%. Knowing the volume and concentration of the added precipitant, calculate the mass of the iodine in the precipitate of AgI and evaluate the activity I_0 of the initial solution.

Simultaneously analyse a sample of the solution containing a mixture of sodium iodide (0.3-1.0 g) and bromide (up to 0.2 g). Put the solution to be analysed in the 50-ml flask. Bring the solution up to the mark and take two 10-ml samples. Add a solution of radioactive NaI (with an activity of 5000 cpm) to the beakers with the solution being analysed, add 10 ml of distilled water and 2 ml of a concentrated solution of NH₄OH. Partly precipitate silver iodide by the action of 6 ml of a 0.05 *M* solution of AgNO₃.

Achieve coagulation of the precipitates, prepare them for measurement, and measure the activity of the preparations obtained so that the relative statistical deviation of the result does not exceed 3%.

Calculate the mass of the iodine in the precipitates and determine the amount of NaI in a control sample.

B. ANALYSIS OF MONAZITE FOR ITS Th CONTENT

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. An ion-exchange column with an anion exchanger (AV-16). An ion-exchange column with a cation exchanger (SBS-KU-2). A sand bath. Conical flasks for 100 ml. Measuring flasks for 250, 100, and 50 ml. Beakers for 200 ml (2). Pipettes for 5 and 25 ml with syringes.

Radioactive Substances. Monazite ore. A standard 0.25 M solution of $\text{Th}(\text{NO}_3)_4$ containing UX_1 (2×10^4 cpm/ml). A 0.25 M solution of $\text{UO}_2(\text{NO}_3)_2$.

Reagents. Solutions: dilute (1 : 1) HCl ; 2 N NaOH ; concentrated, 0.02 and 2 N H_2SO_4 .

Performance of Work

Place a weighed sample of ground (a particle size of about 0.07 mm) ore containing 1 g of thorium into a heat-resistant conical flask, pour in 10 ml of concentrated sulphuric acid, and heat on the sand bath during three hours. Cool the solution, and add 50 ml of water and 5 ml of dilute (1 : 1) hydrochloric acid to it. After stirring the solution with the precipitate during 30 min, decant the solution into a 250-ml measuring flask. Again pour 10 ml of concentrated sulphuric acid onto the remaining precipitate, and repeat the operation of processing the monazite. Filter the solution into the same 250-ml flask, and wash the precipitate several times with dilute hydrochloric acid. Dilute the solution in the measuring flask with water, bringing the volume up to the mark.

Prepare 50 ml of a 0.25 M solution of $\text{Th}(\text{NO}_3)_4$ (a standard solution) and add a solution containing UX_1 . Determine the specific activity of the resulting solution. Mix a known volume (5 ml) of the standard solution with 50 ml of the one being studied (obtained in the processing of the monazite). Partly neutralize the mixture to a pH of about 2 with the aid of an NaOH solution and pass it through the anion-exchange column (diameter 1 cm, height 20 cm) in which the resin has been transformed preliminarily into the SO_4^{2-} form by passing 200 ml of 2-4 N sulphuric acid through it.

Pass the solution being analysed through the column at a rate of 2.5 ml/min. The ions of rare-earth elements are sorbed poorly. For final purification from rare-earth element

cations, pass 100 ml of 0.02 *N* sulphuric acid through the column at a rate of 5 ml/min.

Wash out the thorium from the column by passing 100 ml of 2 *N* hydrochloric acid through it at a rate of 2.5 ml/min. Dilute the solution with water in a 250-ml measuring flask, bringing the volume up to the mark.

Determine the specific activity of the thorium in the solution. For this purpose, measure the activity of an aliquot part of the solution, evaporate it in a bowl for measuring activity, and determine the amount of thorium in the solution by the gravimetric method.

Proceeding from the obtained data, evaluate the total amount of thorium in the weighed sample of the ore taken and its content (in %).

C. DETERMINATION OF Ce IN A MIXTURE OF RARE-EARTH ELEMENT OXIDES

Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window counter. A muffle furnace. A centrifuge. An analytical balance. Beakers for 150 ml (2). Pipettes for 1 ml and 10 ml with syringes. A measuring flask for 50 ml. A funnel with a sintered glass filter No. 3. A crucible. A bowl for measuring activity.

Radioactive Substances. A solution of $\text{Ce}(\text{NO}_3)_3$ containing ^{141}Ce with a specific activity of 37 MBq/g (1 mCi/g).

Reagents. KIO_3 . KBrO_3 . H_2O_2 . A concentrated solution of HNO_3 .

Performance of Work

Prepare a standard solution of $\text{Ce}(\text{NO}_3)_3$ (~ 0.1 *M*) containing ^{141}Ce with an activity of ~ 500 cpm/ml. Determine the specific activity of the solution. To do this, precipitate cerium oxalate from 10 ml of the solution. Filter or centrifuge, roast the precipitate up to CeO_2 , weigh a part of it in the bowl for measuring activity (preliminarily weighed on the analytical balance) and determine the activity in the end-window counter.

Dissolve a weighed sample (~ 1 g) of a mixture of the oxides of rare-earth elements and thorium (with a cerium content of the order of 5-20%) in concentrated nitric acid with heating. Separate the undissolved precipitate by filtration or centrifuging, add to this solution 10 ml of a 0.1 *M*

standard solution containing ^{141}Ce , treat the solution with hydrogen peroxide for transferring the cerium into the + 3 oxidation state, and precipitate the thorium with potassium iodate. Separate the thorium iodate precipitate by filtration or centrifuging, and oxidize the cerium in the filtrate with potassium bromate. Precipitate cerium(IV) with potassium iodate in the form of $2\text{Ce}(\text{IO}_3)_4 \cdot \text{KIO}_3 \cdot 2\text{H}_2\text{O}$. Filter the precipitate and roast it in the muffle furnace to CeO_2 .

Put a part of the roasted and cooled precipitate (approximately equal in mass to the precipitate obtained from the standard solution) in a previously weighed bowl for measuring activity, weigh the sample on the analytical balance and measure its activity. Use the data obtained to calculate the amount of cerium in the weighed sample taken and, proceeding from the mass of this sample, evaluate the content of cerium in the mixture (in %).

D. DETERMINATION OF Pb IN THE PRESENCE OF Ba

In radiochemical practice, it is often necessary to determine lead ions in minerals and rock in the presence of barium ions. This task is easily performed by isotope dilution, whereas its solution by conventional analytical methods is hampered owing to the difficulty of completely separating lead from natural objects. It was exactly when solving this problem that I. Starik developed the method of isotope dilution.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. A drying cupboard. An analytical balance. A lamp for evaporation. An emanator for obtaining an active deposit of thoron. Chemical beakers for 100 ml (3). A porcelain bowl. A funnel. A spatula. A measuring cylinder for 50 ml. A pipette for 1-2 ml with a syringe. A bowl for measuring the activity.

Reagents. $\text{Pb}(\text{NO}_3)_2$. Solutions: saturated—gallic acid; 10% CH_3COONa ; 10% NH_4OH ; 1 *N* and 5 *M* HNO_3 ; 1 *N* HCl .

Performance of Work

Wash off the active deposit of thoron from the platinum plate in the porcelain bowl with a minimum amount of 1 *N* nitric acid containing ~ 0.6 g of $\text{Pb}(\text{NO}_3)_2$. The activity of

the solution should be 3000-5000 cpm. Precipitate lead from the solution in the form of PbCl_2 by adding 1 *N* hydrochloric acid. Filter off the solution, wash the precipitate with a small amount of cold water and dry it.

Weigh two samples each containing about 0.2-0.3 g of $\text{Pb}(\text{NO}_3)_2$ in two 100-ml beakers. Weigh them on the analytical balance with an accuracy up to 0.2 mg. Pour into one beaker the solution being analysed containing a mixture of lead and barium salts (0.2-0.3 g each), and into the other one an equal volume of water.

Add 15-20 ml of a saturated solution of gallic acid and 15-20 ml of a 10% solution of CH_3COONa to the solutions. Should no precipitate appear, add a 10% solution of NH_4OH dropwise until it does appear. Wash the precipitates by decantation with warm water (1-4 times), transfer them with a pipette into weighed bowls for measuring the activity, and dry them during 1.5 h at 110 °C; 100 mg of the dry salt contain 70.8 mg of metallic lead; it has the composition

$\text{Pb}_4(\text{C}_6\text{H}_2\text{O}_3\text{COO})_2 \cdot \frac{1}{2} \text{H}_2\text{O}$. Next add a few drops of 5 *M* nitric acid to the bowls for dissolving the precipitate and uniformly distributing it on the bottom after evaporation. Evaporate the nitric acid under the lamp. Measure the activity of the substances in at least 3.5 h after preparation of the active PbCl_2 . Upon the precipitation of lead gallate, the daughter isotope ThB-ThC completely passes into the precipitate and, consequently, radioactive equilibrium between the ThB and ThC is not violated.

Calculate the specific activity of the PbCl_2 taken for analysis and of the preparation obtained from the solution of the mixture of lead and barium ions. Calculate the content of lead in the solution being analysed.

E. RADIOMETRIC DETERMINATION OF VOLUME OF LIQUID

To determine the volume of a liquid in vessels difficult of access, for example in biological objects (the volume of blood, liquid in an organism), closed reservoirs and the like, it is good practice to use the radiometric method. For this purpose, to a definite volume of a liquid there is added a solution of a radioactive tracer in the same liquid with a known volume specific activity, and after complete mixing, the volume specific activity of the sample is measured. The re-

quired volume is determined from the relation:

$$(V_x + V_0) S_x = S_0 V_0 \quad (17.14)$$

where V_x and V_0 are the required volume and the volume of the added radioactive indicator, respectively, S_0 and S_x are the volume specific activity of the radioactive tracer solution used and that of the sample after mixing, respectively.

Hence,

$$V_x = V_0 \left(\frac{S_0}{S_x} - 1 \right) \quad (17.15)$$

For properly determining the volume, it is essential that the liquid and the added solution of the radioactive tracer be completely mixed and that there be no adsorption of the radioactive isotope nor emergence of it from the system. Measurements must be performed in absolutely identical conditions. To determine the volume of water, tritium water is an ideal tracer that is free of possible losses.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -particles for measuring liquid samples. Pipettes for 1 and 10 ml with syringes. A measuring glass for 10 ml. A vessel with water for measuring the volume.

Radioactive Substances. A solution of Na_2HPO_4 containing ^{32}P with a specific activity of 10 000 cpm/ml.

Performance of Work

Fill the planchet of the counter with distilled water and measure the background. Pour the water out of the planchet, introduce 1 ml of the active solution into it with the aid of the pipette and syringe, add 9 ml of water, and determine the specific activity of the initial phosphate solution. Pour off the active solution from the planchet of the counter into the bottle for waste, thoroughly wash the counter, and again measure the background.

Use a pipette with a syringe to add 1 ml of the initial solution of radioactive phosphate to the vessel containing an unknown amount of water. Let the liquids mix, take 10 ml of the solution using a pipette with a syringe, and immediately measure its activity. Pour the solution from the plan-

chet into the bottle for waste and thoroughly wash the planchet with water, pouring the washing water into the same waste bottle. Evaluate the volume of the water in the vessel.

Note. Transfer the radioactive solution from the vessel whose volume was determined into the waste bottle, thoroughly wash the vessel, and pour the washing water into the same bottle.

Experiment 17.5. DETERMINATION OF MICROAMOUNTS OF IODINE BY THE SUBSTOICHIOMETRIC VARIANT OF THE METHOD OF ISOTOPE DILUTION [7]

The substoichiometric variant of the method of isotope dilution has the advantage over the conventional method that there is no need to determine the amount of the separated element being determined.

Two standard samples of a solution containing m_{st} (in equiv) of the element being determined labelled with a radioactive isotope, with an activity of I_0 , are taken for analysis. The first sample is added to the solution being analysed. The element being determined is separated from the solution being analysed and from the second sample of the standard solution by a substoichiometric amount m (in equiv) of a precipitant. The activity of the samples taken from the solution being analysed (I_1) and the standard (I_2) solutions is measured. The specific activities of the element being sought in the standard solution (S_{st}) and in the one being analysed (S_x) can be expressed as follows:

$$S_{st} = \frac{I_0}{m_{st}} = \frac{I_2}{m} \quad (17.16)$$

$$S_x = \frac{I_0}{m_x + m_{st}} = \frac{I_1}{m} \quad (17.17)$$

Hence

$$m_{st}I_2 = (m_x + m_{st})I_1 \quad (17.18)$$

or

$$m_x = m_{st} \left(\frac{I_2}{I_1} - 1 \right) \quad (17.19)$$

If a radioactive isotope of the element being determined is added to the solution being analysed without a carrier, two identical samples of this solution are taken for determination, substoichiometric amounts m_1 (in equiv) of the reagent are added to it, and then the element being determined bound

to the reagent is separated from the unbound one. Formula (17.10) is used for the calculations. It is transformed for determining the unbound element of interest proceeding from the fact that

$$I_3 = I_0 - I_1 \quad (17.20)$$

where I_3 is the activity of the unbound element being determined. Hence

$$m_x = \frac{m_1}{1 - (I_3/I_0)} \quad (17.21)$$

The element being determined can be separated after the addition of the reagent by precipitation, extraction, or other methods.

The substoichiometric method has a number of variants. Displacement substoichiometry is based on the reaction of displacement by a labelled element being determined in an aqueous solution of another one from a substoichiometric amount of its complex salt in an organic phase. The variant with the use of isotope exchange is based on the exchange of the element being determined between the labelled compound in the solution being investigated and a substoichiometric amount of another readily separated compound of the element being determined introduced into the solution.

In the present experiment, the determination of microamounts of iodine is based on the use of electrodialysis for separating the formed colloiddally dispersed phase of silver iodide from the iodine remaining in the solution.

Equipment and Reagents

Equipment and Utensils. A counter for measuring the radioactivity of preparations of ^{131}I . An arrangement for electrodialysis (Fig. 17.6). A glass flask for 25 ml, four test tubes with a stand, pipettes for taking samples, pincers.

Radioactive Substances. A carrier-free solution of Na^{131}I with a known specific activity of 10^4 cpm/ml.

Reagents. Solutions: NaI (10–100) $\mu\text{g/ml}$; AgNO_3 (100 $\mu\text{g/ml}$); 0.1% Na_2SO_3 . Distilled water.

Performance of Work

Obtain from your instructor a 25-ml measuring flask with a solution containing an unknown amount of sodium iodide. Add to the flask 5 ml of a solution of Na^{131}I without a carrier.

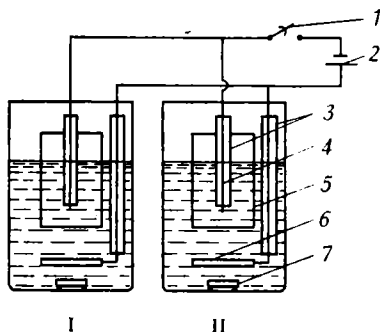


Fig. 17.6. Arrangement for performing electroanalysis:
 I, II—beakers for electroanalysis; 1—switch; 2—d-c source;
 3—electrical insulation of electrodes; 4—cathode; 5—col-
 lodion membrane vessel; 6—anode; 7—magnetic stirrer

Add distilled water up to the 25-ml mark on the flask. Put equal 2-ml samples into two test tubes. Add to one test tube a substoichiometric amount of a silver nitrate solution and to both tubes 1-2 drops of a 0.1% solution of Na_2SO_3 (to eliminate possible oxidation of the iodide ions). Hold the solutions during 40 min to form a colloidal phase. Fill the colloid membrane vessels in the arrangement with equal amounts of the solution from the first and second tubes, respectively, and the beakers with equal portions of distilled water. After this, switch on the voltage across the electrodes of the arrangement. The duration of electroanalysis is 12-13 min.

When this time elapses, take identical amounts of liquid from the glass beakers (~ 1 ml) (I_0 corresponds to the first beaker, I_3 to the second one) and measure the radioactivity of the solutions in a counter (a scintillation counter with an NaI crystal is recommended). Proceeding from the amount of added silver, evaluate m_1 —the amount of iodine in the precipitated colloidal phase (AgI). Find the total amount of iodine in the solution by formula (17.21).

Experiment 17.6. ACTIVATION ANALYSIS [6]

Activation analysis is a new method in analytical chemistry. It is based on irradiation of materials being analysed by neutrons, charged particles, γ -quanta. The result is a nuclear reaction and the formation of radioactive isotopes. The

activity of the latter, their half-life, the type and energy of the radiation, etc. can be used to identify elements and determine their content in the irradiated specimen.

The activity of a formed radioactive isotope by the end of irradiation is determined by the equation

$$A = 6.02 \times 10^{23} m a_{\text{el}} \sigma \frac{1}{A_m} F_0 \times \left[1 - \exp \left(- \frac{0.693 t_1}{T_{1/2}} \right) \right] \quad (17.22)$$

where A is the activity of the formed radioactive isotope by the end of irradiation of the element being determined, disintegration/s, m is the amount of irradiated element, g, a_{el} is the relative content of the isotope being activated in the element, %, σ is the cross section of the nuclear reaction, cm^2 , A_m is the mass of one mole of the element, g, F_0 is the density of the flux of bombarding particles, cps/cm^2 , t_1 is the duration of irradiation, s, and $T_{1/2}$ is the half-life of the radioactive isotope, s.

Equation (17.22) holds in the following conditions:

(1) the flux of bombarding particles does not change during the period of irradiation;

(2) the energy spectrum of the bombarding particles is definite and constant because the reaction cross section depends greatly on their energy;

(3) the initial number of target atoms does not diminish appreciably as a result of the nuclear reaction (this condition is observed virtually always);

(4) the flux density of the bombarding particles does not change appreciably in the volume of the irradiated specimen.

After irradiation, the formed radioactive isotope decays in accordance with its half-life. For known conditions of irradiation, formula (17.22) can be used to calculate the amount of the element being determined in the irradiated target. Such a method in activation analysis is called an "absolute method". But it is rarely used in practice because of the difficulties associated with the determination of the absolute activity. In addition, the accuracy of determining the cross section of nuclear reactions is usually low. The accurate determination of the flux of bombarding particles is also difficult to achieve. All this leads to large errors in analysis (over 40%).

To improve the accuracy of analysis, a relative method is used. In this case, an exactly known amount of the element being determined (a standard) is irradiated together with the specimen being analysed in the same conditions. After irradiation, if required, operations are performed involving the chemical separation (and also radiochemical purification) of the element being determined from the specimen to be analysed and the standard. The activity of specimens of both these preparations are analysed in the same conditions. The amount of the element being determined in the specimen is evaluated from the simple proportion

$$\frac{m_x}{m_{st}} = \frac{A_x}{A_{st}} \quad (17.23)$$

where m_x and m_{st} are the content of the element in the specimen being analysed and in the standard, A_x and A_{st} are the activity of the specimen being analysed and the standard.

The use of the relative method ensures an accuracy of analysis of the order of 10%.

The following methods of activation analysis are distinguished depending on the type of particles used for irradiation: neutron activation analysis, photoactivation analysis based on the reaction (γ, n) , and activation analysis with the aid of charged particles. Each of these methods has its own features and merits, as well as the most favourable fields of application and restrictions.

Among the methods of activation analysis, to date neutron activation analysis has won the greatest recognition and favour in practice. Depending on the energy of the neutrons used, activation analysis with fast neutrons (1-14 MeV) and activation analysis with thermal neutrons (<0.001 MeV) are distinguished. These methods differ first of all in the type of nuclear reactions induced. Irradiation with fast neutrons results most often in reactions of the types $(n, 2n)$, (n, p) , and (n, α) ; irradiation with thermal neutrons produces only the reaction (n, γ) , the only exception being a few of the lightest elements.

One of the chief merits of activation analysis is its high sensitivity (Table 17.1), which in a number of cases cannot be achieved by any other method.

To determine the factors affecting the sensitivity of determination, let us rewrite Eq. (17.22) in another form and

Table 17.1. Sensitivity of Neutron Activation Analysis Using Slow Neutrons of a Reactor with a Flux Density of 10^{12} cps/cm² with Irradiation During 10 h

Elements	Calculated sensitivity of determination, g
Bi, Ca, Fe, S, Si	10^{-6}
Ag, Cr, Hg, Mo, Na, Pt, Ru, Sn, Sr, Te, Tl, Zr	10^{-7}
Ba, Cd, Ce, Co, Cs, Er, Ge, Hf, K, Ni, Os, P, Se, Zn, Y	10^{-8}
Al, Sb, As, Br, Cu, La, Au, I, Pd, Se, Na, Pr, Ta, Tb, Tu, W, Yb	10^{-9}
Ho, In, Mn, Re, Sm	10^{-10}
Dy, Eu	10^{-11}

introduce into it a factor taking into account the decay of the formed radioactive isotope after irradiation:

$$m = \frac{AA_m \exp(-0.693t_2/T_{1/2})}{6.02 \times 10^{23} \sigma A_{st} F_0 [1 - \exp(-0.693t_1/T_{1/2})]} \quad (17.24)$$

where t_2 is the time elapsed from the end of irradiation to the beginning of measuring the radioactivity of a specimen.

A glance at Eq. (17.24) reveals that the minimum discovered amount of an element depends on its individual nuclear characteristics (the isotope composition, isotope activation cross section, the half-life of the formed radioactive isotopes, the atomic mass) and on external factors (the flux of neutrons, the duration of irradiation, the effectiveness of the counter, etc.). The maximum sensitivity is produced by irradiation with thermal neutrons owing to the high cross sections of the reactions (1-1000 barn). The cross section of reactions for fast neutrons is usually much lower (0.001-0.1 barn).

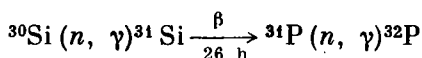
Hence, if one knows the nuclear characteristics of an element, the conditions of irradiation of a specimen, and the procedure used to measure the induced activity, the sensitivity of determination can be evaluated by Eq. (17.24).

The sensitivity of determining elements yielding long-lived radioactive isotopes increases if the duration of irradiation grows.

Another advantage of activation analysis is its high specificity because the radioactive isotope being used for element determination can be identified not only according to the way of its chemical separation, but also according to its half-life and radiation energy.

Like any other method, however, activation analysis also has definite shortcomings and restrictions. One of them is the radiation hazard. To reduce it to a minimum, it is necessary to provide specially equipped radiochemical laboratories and adopt the safety measures needed when working with radioactive substances.

The performing of an analysis is sometimes hindered by the proceeding of competing and secondary reactions. For example, in neutron activation analysis, in addition to the main reaction (n, γ) proceeding on nuclei of the element being determined with the atomic number Z , the reactions (n, p) and (n, α) often proceed that are induced by fast neutrons on nuclei of elements with the atomic numbers $Z + 1$ and $Z + 2$, respectively. As a result of these auxiliary reactions, the same radioactive isotope is formed that is produced by the main reaction. We can cite as an example the determination of phosphorus in silicon. In this case, the main reaction $^{31}\text{P} (n, \gamma)^{32}\text{P}$ is attended by the reaction



This reaction noticeably lowers the sensitivity of determining phosphorus in silicon materials. Generally speaking, for activation with thermal neutrons, the competing and secondary reactions, owing to their small cross sections in comparison with that of the (n, γ) reaction, produce interference only for determining small amounts of elements (impurities) whose atomic numbers differ from that of the main element (the macrocomponent) by one or two units.

In the irradiation of materials having a high capture cross section (Cd, B, Ag, etc.) with thermal neutrons, the effect of self-shielding greatly affects the accuracy of analysis. This effect consists in that the flux of neutrons weakens as it passes into the depth of a specimen owing to the strong absorption of neutrons by the nuclei of the element it contains. This is why the total activity after irradiation is less than it should be in the absence of self-shielding. The neu-

tron flux weakens inside a specimen in accordance with the equation

$$F_x = F_0 (1 - e^{-\sigma Lx}) \quad (17.25)$$

where F_x and F_0 are the flux at a depth of x (in cm) from the surface of the specimen and the incident flux of neutrons, σ is the absorption cross section, cm^2 , and L is the number of atoms in 1 cm^3 of the specimen.

The influence of self-shielding can be eliminated by using small specimens or by diluting liquid or powdery specimens with substances having a small capture cross section.

In the course of development of activation analysis, two fundamental methods took shape that differ in how the irradiated specimens are processed and the final results are obtained, namely, the radiochemical and the instrumental ones.

Initially, the radiochemical method was broadly favoured. It is associated with the chemical decomposition of an irradiated specimen and separation of the activated elements by various techniques. In this case, activation analysis consists of the following steps:

- (1) irradiation of the specimens during a definite time;
- (2) etching to remove surface contaminants (for solid specimens);
- (3) dissolving of the specimens being analysed after the addition of an exactly known amount of a stable carrier;
- (4) carrying out an "oxidation-reduction" cycle for transferring the radioactive isotope and carrier into the same oxidation state;
- (5) separation of the element being determined in the form of a definite chemical compound;
- (6) operations of radiochemical purification;
- (7) measuring the activity of a fraction separated from the specimens being analysed and the standard in identical conditions;
- (8) determination of the radiochemical purity of specimens according to the half-life of the isotope and the energy of its radiation.

Properly planned radiochemical separation makes it possible to determine a large number of elements from one sample and ensures a high specificity, reliability, and sensitivity of the analysis.

In many cases, however, the chemical operations are involved and time-consuming. This is why the instrumental method is used—a method of identifying radioactive isotopes according to their nuclear characteristics (half-life, decay path, radiation energy). When the instrumental method is used, an irradiated specimen without being subjected to chemical processing is delivered directly for measurement.

For the identification and quantitative determination of the activated elements, the activity and the energy of β -particles and γ -rays are measured, and a decay curve is plotted for short-lived isotopes. The scintillation method, chiefly scintillation γ -spectrometry, was found to be very successful for these purposes.

The instrumental methods are simple and rapid. A shortcoming of these methods is the low resolving power of the scintillation spectrometers, which makes their reliable use possible only when relatively simple mixtures of radioactive isotopes are formed in irradiation.

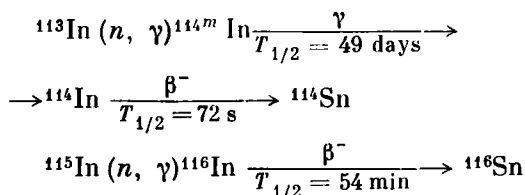
Recent years have seen the greater and greater application of the joint use of the radiochemical and γ -spectrometric methods. This makes it possible to create the most economical and dependable methods of analysing any systems, no matter how complicated they are. The main trend in activation analysis in various fields of science and engineering is the determination of traces of an element. Here the high sensitivity of the method is realized. Another fruitful trend in the development of activation analysis during recent years was the working out of express methods of analysis usually based on the instrumental method. Such express methods are very important when it is necessary to perform large-scale analyses (a search for minerals, analysis and control of products in shop-floor conditions, analysis of biosphere pollution, etc.).

A. DETERMINATION OF In IN SOLID SPECIMENS

This experiment is devoted to the quantitative determination of indium in solid specimens by the method of their activation with slow neutrons.

Natural indium consists of a mixture of two isotopes: ^{113}In and ^{115}In . The following nuclear reactions occur when a natural mixture of indium isotopes is irradiated with

slow neutrons:



The neutron capture cross section in the first reaction is 2.52 barn, and in the second—138 barn. The formation of the isotopes ${}^{114}\text{In}$ and ${}^{116}\text{In}$ is associated with the transition of the nucleus directly into the ground states, bypassing excited levels.

Owing to the short half-life of ${}^{114}\text{In}$, the long half-life of ${}^{114m}\text{In}$, and to the relatively small cross section of the reactions of its formation upon irradiation for a brief period, the main activity in a specimen will be determined by the decay of ${}^{116}\text{In}$.

Equipment and Reagents

Equipment. A counting installation with an end-window counter. A laboratory source of neutrons (10^6 cps). A paraffin block for irradiation.

Reagents. Foil of pure indium. A sheet of the same thickness and density as the indium foil containing an unknown amount of indium.

Performance of Work

Use a laboratory source of neutrons for the experiment (10^6 cps). To retard the neutrons, place the specimen being studied and the standard specimen into the grooves of a transparent thermoplastic or paraffin block (see that both specimens are in the same position relative to the source) and irradiate them during three hours. After this, extract both specimens with pincers from the paraffin block, and measure their activity in identical conditions in the end-window counter. If the specimen being studied contains no impurities having a sufficiently high cross section of the nuclear reaction and has the same dimensions, thickness and density as the standard specimen, the indium does not have to be separated chemically from the specimens.

For more accurate determination of the activity of the

^{116}In , repeat the measurements several times during two hours; plot the logarithm of the activity against the time and use the graph to determine the activity of the specimens at the time when they were removed from irradiation. Calculate the amount of indium in the specimen being studied by formula (17.23).

B. DETERMINATION OF NEUTRON FLUX DENSITY OF A SOURCE

The determination of the neutron flux is actually equivalent to the use of the "absolute method" in activation analysis with all its inherent features. Unlike the absolute method of activation analysis, in the given case we know or can measure a_{el} , σ , m , and A , and do not know the density of the neutron flux F_0 . Transforming Eq. (17.22) relative to the neutron flux density, we obtain

$$F_0 = \frac{AA_m \exp(-0.693t_2/T_{1/2})}{6.02 \times 10^{23} \sigma a_{\text{el}} m [1 - \exp(-0.693t_1/T_{1/2})]} \quad (17.26)$$

To measure the neutron flux density, one must take into account its weakening in the layer of the substance. This may be disregarded if we take a specimen of sufficiently small dimensions (less than 1 mm). In this case, the error in determining the neutron flux density will not exceed 1%.

The main difficulty of the problem lies in the determination of the absolute activity of a specimen of known composition that appears in it under the action of the thermal neutrons of the source being investigated.

Equipment and Reagents

Equipment. A counting installation with an end-window counter (the thickness of the mica in the counter window is 5 mg/cm²). A laboratory source of neutrons (10⁶ cps). A paraffin block for irradiation.

Reagents. Indium standard specimens of various thickness (a set of indium foil specimens). Sheets of aluminium foil of various thickness.

Performance of Work

Put a series of standard specimens made from indium foil of various thickness in identical conditions into recesses of the paraffin block and irradiate them with neutrons from the laboratory neutron source during three hours.

Measure the activity of each specimen by cutting out with a collimator a known (according to the geometric arrangement of the specimen, the collimator, and the detector of radiation) fraction of the flux of electrons from the radioactive specimen. Repeat the measurements 5-7 times during a period equal to two half-lives of ^{116}In . Plot the activity against the time elapsed from the instant of removing the specimen from irradiation, and find its activity at this instant by extrapolation. Use the data obtained to calculate the apparent specific activity of each specimen. Depict the results in the form of a curve of specific activity versus the specimen thickness and extrapolate the curve to the zero thickness of the specimen.

Simultaneously measure the activity of one of the specimens while shielding its radiation with aluminium foil of various thickness. Plot the activity of the standard specimen against the total thickness of the absorbing layer of the substance (in mg/cm^2) between the standard specimen and the counter (the shield, air, the window of the end-window counter). Extrapolate the curve obtained to a zero thickness of the absorbing layer and find the correction factor for the absorption of radiation in the air and the window of the counter.

Evaluate the absolute activity for the chosen specimen:

$$A_t = I_0 k \epsilon s \eta \quad (17.27)$$

where I_0 is the activity measured in the end-window counter and reduced to the instant of removing the specimen from irradiation, k is a coefficient taking into account the absorption and scattering of the radiation in the air and the walls of the counter, ϵ is the coefficient of effectiveness of registering the given kind of radiation by the counter (for β -rays in an end-window counter it is unity), s is a coefficient taking into account the absorption and scattering of the radiation in the material of the specimen (it is determined from the experimental curve of the activity against the thickness of a specimen), and η is the geometric coefficient of the counter of the arrangement:

$$\eta = \frac{\Omega}{4\pi} - \frac{1}{2} \left[1 - \frac{1}{\sqrt{1 + (d^2/4l^2)}} \right] \quad (17.28)$$

where Ω is the solid angle in which β -particles are registered by the end-window counter, d is the diameter of the dia-

phragm aperture, and l is the distance from the plane of the bottom base of the counter to the specimen.

The absolute activity of a specimen determined in this way is used to calculate the density of the neutron flux at the distance where the specimen being studied and the standard specimen are arranged, and from it the flux of neutrons of the source over 4π .

C. DETERMINATION OF In IN A SOLUTION

The present experiment is devoted to a quantitative determination of indium in a solution by neutron activation analysis with the aid of a laboratory source of neutrons. The reactions proceeding in this case are described in Section A of the given experiment.

Equipment and Reagents

Equipment and Utensils. A counter with a scintillation detector (a crystal with a well). A laboratory source of neutrons (10^6 cps). A block for irradiation. Quartz or transparent thermoplastic (Plexiglas) test tubes (6). A pipette for 10 ml with a syringe.

Reagents. A solution of $\text{In}(\text{NO}_3)_3$ containing an unknown amount of In (0.05-0.15 g). Standard solutions of $\text{In}(\text{NO}_3)_3$ containing 0.0025, 0.005, 0.010, 0.015, and 0.020 g of In in one millilitre.

Performance of Work

Put 10 ml of the solution being analysed and standard solutions into each of the quartz (or Plexiglas) test tubes, place them in the cells of the paraffin block, and irradiate them with neutrons during two hours.

Measure the activity of the solution being analysed and the standard solutions in the scintillation counter in the well of the crystal. Calculate the activity at the instant of removing from irradiation. Use the data obtained to plot the activity against the indium content in the standard solutions. Determine the indium content in the solution being analysed according to the calibration graph.

D. DETERMINATION OF Mn

Since natural manganese is the pure isotope ^{55}Mn , the following nuclear reaction proceeds in specimens under the

action of neutrons:



The radioactive isotope formed emits β - and γ -rays. The cross section of the reaction is 13 barns. The half-life of the radioactive isotope ^{56}Mn is 2.59 h.

Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window or scintillation counter. A laboratory source of neutrons with an integral flux of 10^6 cps. A paraffin block for irradiation. Quartz test tubes (6). A measuring cylinder for 25 ml. Porcelain mortars (2).

Reagents. Quartz sand. The specimen being analysed with an unknown content of manganese (0.5-2 g). Standard specimens with a known content of manganese mixed with quartz sand.

Performance of Work

Prepare the specimen to be analysed containing manganese (0.5-2 g) for irradiation. For this purpose, triturate it in a mortar and divide the sample into two approximately equal parts; weigh each part on an analytical balance. Transfer the weighed portions into the mortars, and adding to each of them 5 cm³ of quartz sand measured with the aid of the measuring cylinder, thoroughly triturate the mixture. Pour the powders prepared in this way into quartz test tubes. Place standard specimens containing a known amount of manganese mixed with quartz sand into the other four tubes. Put the standard specimens and those being analysed into the cells of the paraffin block (place the specimens being analysed oppose each other at opposite sides of the block and irradiate them with slow neutrons during three hours).

Upon the completion of irradiation, pour over the contents of the test tubes into standard bowls for measuring the activity and measure the activity of all the specimens in the end-window or scintillation counter. Repeat the measurements several times during two hours.

Plot the logarithm of the activity against the time and use the graph to determine the activity of the specimens being studied and the standard ones at the instant of their removal from irradiation.

Plot the activity of the standards against their manganese content. Use the graph to determine the amount of manganese in the specimens being analysed. Evaluate the manganese content in the initial specimen (in %).

E. PHOTOACTIVATION DETERMINATION OF OXYGEN IN Be AND Ti

It is very important in modern engineering to determine the oxygen content in a number of metals because small impurities of oxygen greatly affect their physicochemical properties. To date there are no more or less satisfactory physicochemical methods; only activation analysis made it possible to develop express methods for determining oxygen in metals:

(1) activation with fast neutrons according to the reaction $^{16}\text{O}(n, p)^{16}\text{N}$ ($T_{1/2} = 7.4 \text{ s}$, $E_{\beta^+} = 4\text{--}10 \text{ MeV}$, and $E_{\gamma} = 6\text{--}7 \text{ MeV}$);

(2) photoactivation according to the reaction $^{16}\text{O}(\gamma, n)^{15}\text{O}$ ($T_{1/2} = 2.1 \text{ min}$, $E_{\beta^+} = 1.6 \text{ MeV}$, there is no γ -radiation).

Both methods have the same sensitivity—of the order of $10^{-3}\%$.

The present experiment is devoted to the photoactivation determination of oxygen in beryllium and titanium. Upon irradiation with γ -quanta, beryllium is not activated.

Titanium according to the reactions $^{50}\text{Ti}(\gamma, p)^{49}\text{Sc}$ and $^{48}\text{Ti}(\gamma, n)^{47}\text{Ti}$ forms two isotopes with half-lives of 58 min and 3.2 hours, respectively. In this connection, the sensitivity of determining oxygen lowers to $\sim 10^{-2}\%$.

A number of processes are possible when γ -quanta interact with atomic nuclei: the excitation of higher levels of a nucleus, nuclear reactions of the type (γ, n) , (γ, p) , (γ, α) , etc. All the photonuclear reactions are threshold ones, i.e. they proceed only under the action of sufficiently hard γ -quanta. Another feature of photonuclear reactions is their resonance nature. Beginning from the threshold energy, the cross section of a photonuclear reaction rapidly increases with a growth in the energy of the γ -quanta up to a certain maximum value, and then drops again. Of all the photonuclear reactions, the reaction (γ, p) , which is in the greatest favour in photoactivation analysis, has the smallest

value of the threshold and the largest value of the cross section. The reaction (γ , n) usually results in the formation of a neutron-deficient isotope of the initial element that decays by the emission of positrons. The thresholds of the reactions (γ , n) for most elements range from 6 to 16 MeV.

Two kinds of electron accelerators are mainly used as sources of hard radiation: a linear accelerator of electrons and a betatron. The latter is a simpler and more available source of γ -radiation with an energy of 10-30 MeV.

Electrons are accelerated in a betatron under the action of an eddy electric field induced by a varying magnetic field in a vacuum accelerating chamber. The electrons, accelerated to the required energy, are directed onto a target made from a heavy metal, and hard bremsstrahlung (braking radiation) appears. The energy distribution of the γ -radiation appearing upon the braking of monochromatic electrons is continuous and extends from zero to the maximum energy virtually equal to the energy of the accelerated electrons. The intensity of radiation in the braking spectrum is inversely proportional to the energy of the emitted γ -quanta. The bremsstrahlung of a betatron has a sharply expressed spatial asymmetry and is a narrow slightly diverging beam of γ -quanta directed to the same side as the beam of electrons being accelerated.

A betatron can be used for irradiation in two ways: outside the acceleration chamber of the betatron (an external target) or inside it (an internal target). Irradiation with the aid of an internal target makes it possible to obtain a density of the γ -quantum flux that is 100-500 times greater than upon irradiation outside the chamber, and this, in turn, provides a higher sensitivity of determination. Specimens having a small size (0.15-0.20 cm³) can be irradiated with the aid of an internal betatron target. Unfortunately, the stability of the betatron flux intensity is not high (of the order of 30%), which is why a monitor has to be employed for controlling the intensity of radiation.

The oxygen radioactive isotope ¹⁵O formed upon photoactivation has such a short half-life that the use of chemical methods is virtually impossible. This is why analysis has to be performed by the instrumental method with the use of physical ways of identification and quantitative determination of the activated elements.

Photoactivation analysis is featured by the fact that as

a result of irradiation, short-lived β^+ -emitters are often formed that decay without an attending γ -radiation or with a small yield of γ -rays, while the annihilation γ -radiation has the same energy (511 keV) for all positron emitters. Consequently, scintillation γ -spectrometry cannot be used in this case. The spectroscopy of γ -radiation with the use of thick specimens is difficult to perform owing to the distortion of the shape of the spectrum. In this connection upon the photoactivation determination of oxygen in beryllium and titanium, the method of analysing the curve of a specimen's activity decay is employed. The radioactive isotopes are identified according to their half-life.

Equipment and Reagents

Equipment. Two counters with a detector of β -radiation. A betatron (25 MeV).

Reagents. Standard specimens of beryllium or titanium containing a known amount of oxygen (0.2-4%). A monitor—a preparation of a metal with a large oxygen content. Specimens of a metal for analysis.

Performance of Work

Prepare a monitor from chemically pure beryllium with a high oxygen content. Prepare the specimens to be analysed and the monitor in the form of disks 16 mm in diameter, 1-1.5 mm thick, and with a mass of 0.5-1 g. Depending on the form in which the metal is, either machine such disks on a lathe or fabricate them by pressing under a pressure of 5-9 tonne/cm² from a powder or shavings.

Prepare the standard specimens by pressing a powder or shavings of the relevant metal subjected to a various degree of oxidation in the process of heating in air at a temperature of 400-500 °C. Determine the amount of introduced oxygen by the gravimetric method according to the increase in the mass of the powder or shavings in the process of oxidation. Vary the concentration of oxygen in the standard specimens from 0.2 to 4%.

Irradiate the standard specimens and the monitor during six minutes, and then the specimen being analysed with the monitor after rigidly fastening the disks close to one another in the holder introduced into a "pocket" in the internal target of the betatron.

In one minute after the completion of irradiation, measure the activity of the specimen being analysed or the standard specimen and the monitor. Do this continuously with the aid of two counters that are alternately (every 30 s) connected to the detector of radiation. During the operation of one counter, record the readings of the other one and prepare it for repeated registration of the activity.

Plot the change in the activity of all the specimens and the monitor in time. Next according to the experimental curves of the decrease in the activity with time, separate by graphical analysis a straight line with a half-life of 2.1 min according to which find the activity of the ^{15}O . Find the activity of the oxygen at the instant of removing the specimens and monitor from irradiation.

To eliminate the difference in the density of the flux of γ -quanta in each individual irradiation, relate the activity of the oxygen in the standard specimens and in the one being analysed at the end of irradiation to the activity of the simultaneously irradiated monitor:

$$K = A_S/A_M$$

where A_S and A_M are the activities of the oxygen in a specimen and in a monitor at the instant of removing from irradiation, respectively.

Plot a calibration graph showing the values of K for the standard specimens against the oxygen content in them. Using the found value of K for the specimen being analysed from the calibration graph, determine the oxygen content in it.

Experiment 17.7. DETERMINATION OF B ACCORDING TO THE ABSORPTION OF NEUTRONS [1]

A number of isotopes have a great ability of absorbing slow neutrons. Such isotopes are contained in the natural isotope mixture of cadmium, boron, lithium, etc. The number of neutrons retained by a specimen containing an isotope is proportional to the number of atoms of the given isotope. Consequently, the weakening of the intensity of a neutron beam can be used to appraise the content of an element in natural specimens.

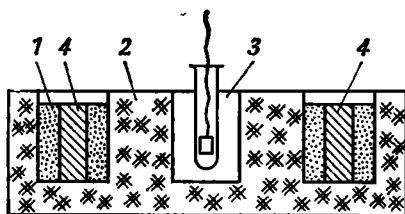


Fig. 17.7. Block for determining the boron content according to the absorption of neutrons:

1—mixture being analysed; 2—paraffin block; 3—well for source of neutrons; 4—detector of neutrons

The weakening of the intensity of a neutron beam can be determined by comparing the activity of a readily activated substance (a "detector") upon direct irradiation and upon irradiation by a flux passing through a layer of the specimen being analysed.

The determination of boron according to the absorption of neutrons is a highly sensitive method owing to the large capture cross section of thermal neutrons by nuclei of ^{11}B according to the equation $^{11}\text{B}(n, \alpha)^8\text{Li}$. The isotope ^7Li has a half-life of 0.875 s and therefore cannot be used for measuring the boron content in a specimen according to the activity of the product formed.

Elements such as Dy, Ag, Rh, and Mn with a high neutron capture cross section that yield radioactive isotopes with kinds of radiation and half-lives convenient for measurement can be used as a detector of slow neutrons. Manganese, for example, has a neutron capture cross section of 11.5 barn and by the reaction $^{55}\text{Mn}(n, \gamma)^{56}\text{Mn}$ forms a radioactive isotope with a half-life of 2.59 h that emits β - and γ -rays.

The experiment is run with the aid of blocks (Fig. 17.7) with special planchets where the substance being analysed with a large capture cross section of slow neutrons is placed; the detector is placed in the inner cylinder of the planchet. In activity measurements, the detector is extracted from the planchet and inserted into the well of a scintillating monocrystal.

A flux of neutrons with thermal speeds can be obtained by retarding fast neutrons from laboratory sources of neutrons in a layer of paraffin 5-6 cm thick.

The accuracy of determining the boron content and the

sensitivity of the method depend on the flux of neutrons of the source. For a source emitting 10^6 cps, the sensitivity of determination is $\sim 1\%$.

Equipment and Reagents

Equipment and Utensils. A counter with a scintillation detector. A laboratory source of neutrons (10^6 cps). A paraffin block for irradiation. Planchets (8) for the specimens being analysed and the standard ones (with manganese dioxide in the inner cylinder). A measuring cylinder for 100 ml. A porcelain mortar.

Reagents. A set of standard specimens with a known boron content (0.01-0.3 g). A specimen to be analysed with an unknown (0.03-0.3 g) content of boron. Quartz sand.

Performance of Work

Triturate the sample of the substance (or mixture of substances) to be analysed with an unknown boron content (0.03-0.3 g) in the mortar. Divide the specimen into two parts and weigh each part on an analytical balance. Transfer each of the weighed portions into the mortar, and after adding 50 cm³ of quartz sand measured with the aid of the measuring cylinder, again thoroughly triturate the mixture. Pour the mixtures prepared in this way into the planchets for the specimens being analysed. Place the planchets with the standard specimens and those being analysed into the block for irradiation. Place the specimens being analysed opposite each other at opposite sides of the block. Irradiate them during two hours.

Upon the termination of irradiation, measure the activity of the manganese detectors in the scintillation counter. Measure the activity of each detector during 4 min (reduce the counting rate of the measured detectors to the time of removal from irradiation). Use the activity of the detectors and the boron content in the standard specimens to plot a calibration curve of the counting rate against the amount of boron.

Using the curve, determine the amount of boron in the specimens being analysed. Calculate the boron content (in %) in the initial material. Proceeding from the statistical variance of the data of the calibration curve, appraise the accuracy of the method.

Experiment 17.8. DETERMINATION OF Be BY THE PHOTONEUTRON METHOD [2]

The photoneutron method of chemical analysis consists in registering the neutrons emitted by nuclei under the action of γ -radiation. The nuclei of atoms of the chemical elements have various binding energies of the nucleons. The photoneutron method is convenient in practice for determining the chemical elements in which the binding energy of the nucleons is low. For the majority of elements, the binding energy is ~ 8.5 MeV and below. Beryllium has the smallest binding energy of its nucleons—1.666 MeV, and next comes deuterium—2.226 MeV. When γ -radiation with an energy exceeding the binding energy acts on beryllium, the nuclear reaction ${}^9\text{Be}(\gamma, n){}^8\text{Be}$ proceeds.

In performing an analysis for the content of beryllium, one must exclude the influence of the neutrons emitted in the reaction ${}^2\text{H}(\gamma, n){}^1\text{H}$. For this purpose, it is essential that the energy of the exciting γ -radiation be lower than the binding energy of the nucleons in a deuterium nucleus and higher than that in a beryllium one, i.e. 1.7–2.2 MeV. The isotopes that can be used for preparing sources of γ -radiation in the photoneutron determination of beryllium are given in Table 17.2.

Table 17.2. Sources of γ -Radiation for the Photoneutron Determination of Beryllium

Source of γ -radiation	Radiation energy, MeV	Half-life	Mean energy of photoneutrons, MeV
${}^{124}\text{Sb}$	1.7, 2.1	53.7 days 60.4 days	0.024
${}^{88}\text{Y}$	1.85, 2.76	105 days	0.158
${}^{56}\text{Mn}$	1.8, 2.65, 2.13	2.6 h	0.15, 0.3
${}^{72}\text{Ga}$	1.88, 2.20, 2.50	14 h	0.78
${}^{140}\text{La}$	2.535	40.3 h	0.62
MsTh_1	2.614	6.7 years	0.827
${}^{21}\text{Na}$	2.75	14.9 h	0.83

With respect to the energy characteristics, the radioactive isotope of antimony ${}^{124}\text{Sb}$ will be the most suitable; its only shortcoming is its comparatively short half-life. An impor-

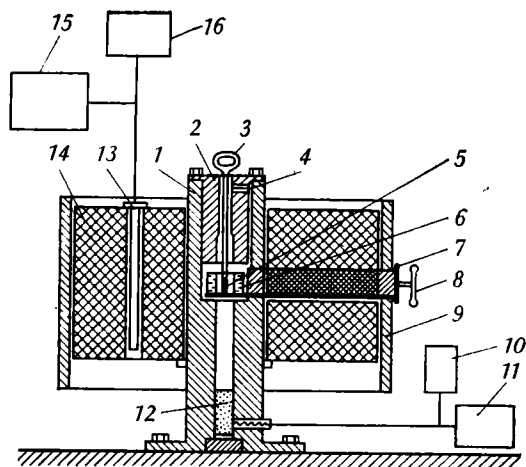


Fig. 17.8. Installation for determining beryllium by the photoneutron method:

1—lead housing; 2—bearing housing; 3—rod; 4—fixing device; 5—source of γ -radiation; 6—vessel with substance being studied; 7—extensible table; 8—handle; 9—lead shielding; 10, 15—power packs of counters; 11—registering instrument; 12—counter of γ -radiation; 13—boron counters; 14—container; 16—instrument for registering neutrons

tant merit of it is the large yield of γ -quanta whose energy exceeds the threshold of the photoneutron reaction for beryllium.

In performing photoneutron analysis, one must bear in mind that the neutrons are registered when a flux of γ -radiation is present. The neutron detectors used must have a very low effectiveness to γ -quanta or produce electric signals of a considerably lower amplitude when they enter the detector than when neutrons do. This can be achieved (with the provision of an amplitude discriminator), for example, in boron proportional counters (the intensity of the background is 1-6 cpm at a power of the dose from the source of γ -radiation of 2.6×10^{-6} C/kg (10^{-2} R/s). In addition to proportional counters, scintillation counters may be used with the phosphor in the form of a thin film containing lithium or boron.

The laboratory arrangement (Fig. 17.8) consists of lead housing 1 intended to protect the experimenter from the action of γ -radiation. Source of γ -radiation 5 has the form

of a cylinder fastened on rod 3 that can occupy one of two positions in height. This is ensured by the provision of spherical fixing device 4 in bearing 2. In the lower (working) position, source 5 enters annular working vessel 6 containing the substance being analysed. In its upper position, the source emerges completely from vessel 6. The latter is on extensible table 7 and can be extracted outward with the aid of handle 8.

For constantly monitoring the change in the intensity of source 5, housing 1 accommodates counter 12 of γ -radiation connected to an external registering instrument 11. Container 14, filled with paraffin for retarding the neutrons, is arranged on the middle part of the housing. The container is provided with several vertical ducts equidistant from the centre of the source that accommodate proportional boron counters (type SNMO-5). Boron counters 13 are connected in parallel to the general electric outlet from the registering instrument provided with an amplitude discriminator (for example, SCh-3). An increase in the number of counters is useful for improving the sensitivity of the arrangement, but this is attended by an increase in the background. For example, when four boron counters are used, the source of γ -radiation is ^{124}Sb [4×10^3 MBq (100 mCi)], and the specimen being studied has a mass of 100 g, the sensitivity of the arrangement reaches $4 \times 10^{-4}\%$ of Be at a background of 3-5 cpm.

To improve safety in work, the arrangement is additionally surrounded by lead walls 9 whose thickness is chosen depending on the characteristics of the source of γ -radiation used.

The concentration of the beryllium in the solution being analysed (in g/litre) is calculated by the formula

$$c = c_{\text{st}} \frac{I}{I_{\text{st}}} \quad (17.29)$$

where c_{st} is the content of beryllium in the standard solution, I and I_{st} are the counting rate (minus the background) of the preparation being analysed and of the standard one, respectively.

When analysing loose substances, the specimens are also placed in the working vessels. To observe identical geometric conditions, the standard preparation and the one being analysed must be in vessels at the same level. The beryllium

content in the product being analysed (in %) is determined by the formula

$$c_x = c_{st} \frac{I_{mst}}{I_{stm}} \quad (17.30)$$

where m_{st} and m are the mass of the standard preparation and of the one being analysed, respectively.

To improve the accuracy of measurements, it is desirable to have standard specimens that are close in chemical composition and density to the specimen being analysed. Solutions with a known content of beryllium oxide in concentrated sulphuric acid may be used as liquid standard specimens. Solid standard specimens are prepared from a filler of suitable characteristics and a definite amount of beryllium oxide that are trituated to a particle size of 0.1-0.07 mm and are thoroughly stirred.

A number of specific errors appear in the photoneutron determination of beryllium. An error because of the absorption of photoneutrons by the filler substance appears if it includes elements with large neutron capture cross sections such as B, Li, Cd, and rare-earth elements. The maximum error due to this phenomenon is estimated in the given arrangement experimentally. For this purpose, the activity of the standard beryllium preparation, in which there are virtually no elements with a large neutron capture cross section, is measured. Next the same preparation is placed behind a cadmium screen 1 mm thick that absorbs thermal neutrons. The maximum possible error is determined by the ratio of the difference between two measurements related to the first result. This error usually fluctuates from 4 to 16% depending on the number of counters used, their arrangement, and also the shape and dimensions of the preparation being measured.

With small amounts of the substance being analysed, the error due to the absorption of photoneutrons by the filler sharply diminishes, but the sensitivity of the method also drops simultaneously. With large amounts of the substance being analysed, the sensitivity of the method increases, but the error grows simultaneously because of lowering of the energy of γ -radiation of the source in the substance of the sample being analysed. This is especially appreciable when the materials of the standard and the preparation being analysed appreciably differ in their density and mean atom-

ic number. The maximum errors caused by this phenomenon may be several per cent. When large working vessels are used and elements with high values of the capture cross sections of slow neutrons are present, the data of several measurements performed in similar conditions, but in working vessels of a different volume filled to the same level, are used. For two measurements, the result (in %) can be evaluated by the formula

$$c_x = c_s \frac{c_s - c_l}{d_l - d_s} d_s \quad (17.34)$$

where c_s and c_l are the concentrations of beryllium determined when measuring preparations of an identical chemical composition in a small and a large working vessels, respectively, and d_s and d_l are the thickness of the layers of the substance in these vessels.

In the proper planning of the experiments, the errors of analysis are approximately within the following limits:

(1) errors due to the absorption of neutrons and γ -radiation of the source by the material of the filler—1-2%;

(2) errors in analysis of the standard specimens—1-2%;

(3) errors due to the inaccuracy of determining the geometric conditions of measurement—1-2%;

(4) errors associated with the measuring apparatus (if the counting rate is not over 3000 cpm)—0.8-1.5%.

At a duration of measurement of 25 min and a background of 1 cpm, the minimum counting rate registered by the instrument will be 2 cpm, which corresponds to the sensitivity at which 1 mg of BeO can be determined [the activity of the source is $\sim 4 \times 10^3$ MBq (~ 100 mCi)].

Equipment and Reagents

Equipment and Utensils. An installation for photoneutron analysis (see Fig. 17.8). A cadmium screen. A set of working vessels.

Reagents. Solid and liquid standard specimens.

Performance of Work

Connect the installation to electric mains and warm it up during 30 min. Change the voltage on the neutron counter and, by adjusting the threshold of discrimination in the installation, achieve the optimal conditions of its operation

according to the relevant instructions*. Measure the background: in a properly functioning installation it must never exceed 1-6 cpm depending on the number and type of detectors employed.

Using extensible table 7 (see Fig. 17.8), introduce the working vessel with the control preparation into the installation and check its operation. Lower the rod with source 5 of γ -radiation into its bottom (working) position. Use counter 12 and external registering instrument 11 to appraise the density of the source of γ -radiation.

Extract the control preparation from the installation. Pour the solution to be analysed into a working vessel having a large diameter and place the vessel into the installation. After performing measurements with the solution being analysed, carry out similar experiments with a standard solution, which is taken in the same volume and poured into an identical working vessel. Calculate the beryllium concentration.

Measure the activity of the same preparations in working vessels of a smaller diameter. Determine the amount of beryllium with a view to the absorption of slow neutrons by the material of the filler. Using a cadmium screen, find the maximum error due to the absorption of slow neutrons by the material of the filler. Determine the sensitivity of the method corresponding to the conditions of the experiment. Compare the data obtained with the known results of chemical analysis.

Experiment 17.9. DETERMINATION OF CHEMICAL ELEMENTS ACCORDING TO THE RADIATION OF THEIR NATURALLY RADIOACTIVE ISOTOPES

To determine the content of radioactive elements or chemical elements containing radioactive isotopes in a natural mixture, three methods can be used. In the first one, the absolute activity is determined according to the

* Before performing measurements, check the proper functioning of the electrical equipment of the installation during several days by measuring a calibration preparation containing beryllium that ensures a counting rate of 2000-3000 cpm. The reproducibility of the results of measurements performed on different days must be within 2-3%.

radiation of a definite energy. Next the known scheme of decay is used to calculate the content of the radioactive element. In the second method, relative determinations are performed by comparing the activity of the specimen being analysed with that of standard specimens; the measurements are performed in completely identical conditions. This method is simpler, more accurate, and in this connection has found greater favour. The third method consists in determining the amount of the daughter element accumulated from the parent one in a definite period of time.

The present experiment is devoted to the determination of potassium according to its natural radioactivity by the second method. The latter is very simple, and therefore when no high accuracy is needed, it competes successfully with the analytical methods.

A natural mixture of potassium isotopes contains 93.08% of ^{39}K , 6.91% of ^{41}K , and 0.0118% of ^{40}K . Potassium-40 is a radioactive isotope. Its half-life is 1.415×10^9 years. The β -rays it emits have a maximum energy of 1.33 MeV. In addition to β -decay, 12% of the decays occur by the capture of an orbital electron (K -capture).

Owing to the constancy of the isotope composition, the content of potassium in a specimen can be assayed according to its radioactivity. Since the content of ^{40}K is low, while its half-life is large, the activity of specimens containing potassium can be measured well only if large samples are used and if the counter has a large angle of subtending the sample. This is why it is necessary to measure large samples in which the absorption of the β -radiation is observed. The path of β -particles of ^{40}K can be evaluated by the formula

$$R_{\max} = 0.54E_{\max} - 0.15 \quad (17.32)$$

When $E_{\max} = 1.33$ MeV, the path is 0.55 g/cm^2 .

At a density of powdered samples of $\sim 2 \text{ g/cm}^3$, the layer of complete absorption, for example in KCl, will be $\sim 3 \text{ mm}$, consequently, layers of a different thickness exceeding 3 mm will yield a β -activity proportional to the potassium content if the geometric arrangement of the specimens relative to the counter is the same. This circumstance is extremely convenient because it does not require an identical density of the layer in various samples.

When using a Geiger-Müller β -counter for measurements, the counting rate may increase somewhat at the expense of

the γ -rays with an energy of 1.45 MeV (in the conditions of our measurements) attending the K -capture. But the rate of counting caused by the γ -rays is approximately proportional to the total content of ^{40}K in a sample, and with close densities of the sample—to the percentage of the potassium content. With sufficient experience, one can determine the amount of potassium with a relative error of 10% at its content of 3-5%.

To determine the potassium content according to ^{40}K by relative methods, it is first necessary to plot the counting rate against the amount of potassium in a sample (a calibration graph). Next the counting rate is determined for a sample and the graph is used to find the potassium content in it (in %).

The amount of potassium in a sample can also be found by other methods, after having determined the absolute specific activity of a sample.

For β -radiation, we have

$$I_s = (s'S)/\mu \quad (17.33)$$

where I_s is the activity of the saturated layer registered by the counter, cpm, s' is the surface area of 1 g of the sample, cm^2 , S is the specific activity, cpm/g, and μ is the absorption coefficient in the material of the sample, cm^2/g .

In our case

$$s' = \pi r^2 + 2\pi rH \quad (17.34)$$

where r is the radius of the sample, and H is its height.

The obtained value of the specific activity S can be used to calculate the value of the specific activity S_0 expressed in the units dps/g:

$$S_0 = S/(\eta\epsilon ksq) \quad (17.35)$$

where η is the geometric coefficient of the counter, ϵ , k , s , and q are coefficients taking into account the effectiveness of counting β -particles, the fraction of β -particles absorbed along the path to the counter, absorbed in the substance of the sample, and getting into the counter because of reflection from the substrate of the preparation, respectively.

Equipment and Reagents

Equipment and Utensils. A counting installation with a scintillation detector in the form of a thin organic film or with a Geiger-Müller β -counter. A slide caliper for measuring the dimensions of samples-

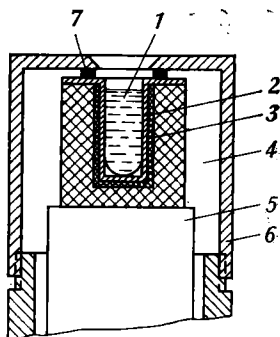


Fig. 17.9. Arrangement for registering the radioactivity of ^{40}K by the scintillation method:

1—active sample; 2—aluminium foil screen; 3—film of a scintillator; 4—Plexiglas light duct; 5—photoamplifier; 6—light-protecting case; 7—rubber gasket

Special measuring vessels with thin walls. A funnel for pouring the substances being studied into the vessel. A mortar.

Reagents. Mixtures of KCl and NaCl with 10, 30, 40, and 53% of potassium. $\text{K}_2\text{S}_2\text{O}_8$. K_2CrO_4 . $\text{K}_2\text{Cr}_2\text{O}_7$. A sample with an unknown content of potassium.

Performance of Work

Measure the activity of the potassium in a scintillation counter with a large angle of subtending of the specimen. Owing to the use of a scintillator in the form of a thin film, only β -radiation is registered, and the correction for γ -radiation is reduced to a minimum. Figure 17.9 shows a schematic view of a scintillation transducer.

Place specimen 1 into a special vessel made from a thin polyethylene film ($\sim 4\text{--}5 \text{ mg/cm}^2$) and put it into a well lined with film 3 of a scintillator (*n*-terphenyl in polystyrene). To prevent light getting in, close the scintillator with thin aluminium foil (about 2 mg/cm^2). The absorption of the β -particles in the material of the vessel and the protective aluminium film does not appreciably affect the measurement results.

When a Geiger-Müller counter is employed, use the measuring vessel shown in Fig. 17.10. The inner wall of the vessel facing the counter is so thin ($5\text{--}6 \text{ mg/cm}^2$) that the absorption in it may be disregarded. In these cases, all the correction coefficients may be assumed to be close to 1,

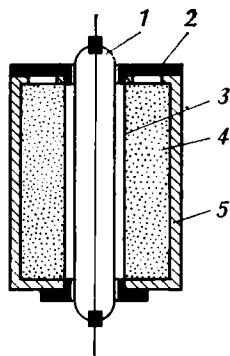


Fig. 17.10. Measuring vessel for registering the radioactivity of ^{40}K with a Geiger-Müller counter:

1— β -particle counter; 2—upper ring of vessel; 3—rubber or cellophane film with a thickness of 5-6 mg/cm²; 4—substance being analysed; 5—outer wall of vessel

and, consequently, $S_0 = S$. Determine the background of the counter by filling the measuring vessel with pure NaCl. Measure the activity of the samples of the mixtures of NaCl and KCl with a potassium content of 10, 20, 30, and 40%, and also the activity of pure KCl. First triturate the samples in the mortar. Use the data obtained to plot a calibration graph.

Measure the activity of the pure salts $\text{K}_2\text{S}_2\text{O}_8$, K_2CrO_4 , and $\text{K}_2\text{Cr}_2\text{O}_7$. Determine the potassium content according to the graph and compare it with the content evaluated according to the chemical formula of the given compound. Use the calibration graph to determine the content of potassium in the control sample with an unknown composition.

Calculate the potassium content in the studied samples proceeding from the activity measurements, the half-life of ^{40}K , the content of ^{40}K in an isotope mixture of potassium, the composition of the radiation, the surface area, and the self-absorption coefficient ($\mu = 8.9 \text{ cm}^2/\text{g}$) using the formulas given above. Compare with the result obtained graphically.

Experiment 17.10. RADIOCHEMICAL ANALYSIS OF NATURAL OBJECTS [8, 9]

Great attention is given to the radiochemical analysis of natural objects in connection with the pollution of the biosphere by radioactive substances as a result of nuclear

tests and because of the activities of industrial enterprises using radioactive isotopes. These contaminants, especially long-lived fission products of heavy element nuclei (such as ^{90}Sr or ^{137}Cs) are a great hazard because they readily enter the biological cycle and together with water or food products enter a human organism and may accumulate in it. This is why the determination of the content of radioactive isotopes in objects of the environment is an important sanitary and hygienic task.

A. TAKING OF SAMPLES AND PRELIMINARY PREPARATION OF A MATERIAL FOR RADIOCHEMICAL ANALYSIS

Equipment and Reagents

Equipment and Utensils. A muffle furnace. A drying cupboard. A water bath. A set of sieves. A bathometer. Cans, cylinders, beakers, and bottles of polyethylene. Planchets for collecting samples of radioactive precipitations (of stainless steel, aluminium, polyethylene, enamelled). Chromatographic columns of various sizes. Porcelain bowls and crucibles for 0.5-0.2 litre. Nickel or iron bowls and crucibles for 0.5 and 0.2 litre. Beakers for 1, 0.5, and 0.2 litre. Measuring cylinders. A Büchner filter. A platinum bowl for 0.5 litre.

Radioactive Materials. Samples of precipitations, soils, water, biological material intended for analysis.

Reagents. Cation exchanger KU-2 (H^+ form). Anion exchanger AV-17 (Cl^- form). (The ion exchangers are prepared for work according to the procedure described in Chap. 3 of Vol. 1.) KNO_3 . Na_2CO_3 . KOH . Solutions: concentrated H_2SO_4 ; concentrated, 6 M , 0.5 and 0.3 N HCl ; concentrated (fuming) H_2SO_4 with a density of 1.5 g/cm^3 ; 0.5 M oxalic acid; 3% H_2O_2 ; 0.2 M of Sr , Ce , Cs , and Ru chlorides or nitrates; 50% Na_2CO_3 ; concentrated H_2F_2 .

Performance of Work

(a) Taking of Samples

Water. In accordance with the objects of the investigation, samples of water sources may be taken from various depths of a water basin. Use bathometers for taking samples in these cases. To prevent the adsorption of radioactive isotopes on the walls of the vessel, acidify a sample taken (~ 10 ml of concentrated HCl or HNO_3 per litre of water) and store it in a polyethylene or plastic container. Depending on the level of radioactivity, the volume of the sample should range from 1-1.5 to 10-30 litres and more.

Soil. Take samples of the soil from various points of the area being investigated and then thoroughly stir the mixture. Since the content of radioactive isotopes varies very greatly with the depth, always take the "mean sample" from a definite depth.

Biological Objects (plants, bones, milk, grain, etc.). Whenever possible, also prepare a mean sample. Differential analysis is often used: the content of radioactive isotopes is studied either in plants of one species, or only in a certain part of a plant (in the roots, stems, leaves, etc.).

Radioactive Precipitations. To collect radioactive substances precipitating from the atmosphere, use collecting means with a definite collecting area—cupped planchets, high-wall vessels, horizontal planchets, contrivances with columns filled with ion-exchange resins.

It is convenient to gather atmospheric precipitation by using inclined areas of a definite size covered with a plastic compound.

(b) Preparing Samples for Analysis

After taking a sample, the next task is to transfer it into a solution (if the sample is solid) and concentrate the radioelements contained in it in a minimum volume (for water, precipitations, milk, and the like).

Water. When analysing water for its content of separate radioactive isotopes, especially only slightly active water of about 4 Bq/litre ($\sim 10^{-10}$ Ci/litre), quite substantial volumes of it have to be taken. Evaporation of such amounts alone takes too much time and leads to considerable losses of the radioactive isotopes (at the expense of adsorption, evaporation, and for other reasons). This is why the radio-nuclides have to be concentrated, for which purpose the methods of electrodialysis, coprecipitation, evaporation, and ion exchange have to be used. Especially good results are achieved when using the method of ion exchange on strongly acid cation exchangers and strongly basic anion exchangers.

Fill a chromatographic column (35 cm long and 4.5 cm in diameter) with a preliminarily swollen cation exchanger KU-2 and pass 50-100 litres of water through it at a rate of 6-8 litre/h. For each 20 litres of water, preliminarily add carriers containing 50 mg each of Ce and Cs and 400 mg

of Sr (in the form of chlorides and nitrates) and 50 ml each of hydrochloric acid.

Next desorb the Ce with 500 ml of 0.3 *N* hydrochloric acid, the Sr and other cations with 6 *M* HCl (3-4 litres). Evaporate the hydrochloric acid filtrates obtained up to 50-100 ml, after which perform the required separations*.

Soil. When determining the content of radioactive isotopes—fission products—in soils, the main problem is the most complete extraction of a radioactive element from large samples. Such a method of treatment of the soil has to be chosen that would make it possible to extract the radioactive element of interest to us without appreciable impurities of another radioactive element.

The radioactive isotopes of Sr and Ce are virtually quantitatively (by 99%) extracted when soil is treated with dilute solutions of mineral acids, and the radioactive isotopes of Zr and Nb with a solution of 0.5 *M* $\text{H}_2\text{C}_2\text{O}_4$ and 1 *N* HCl. The isotopes of Cs and Ru can be extracted with sufficient completeness only after destroying the silicate structure of the soil, which is achieved by prolonged boiling with 9 *M* sulphuric acid or by melting with strong oxidizing agents. Below is given the procedure for preparing and preliminarily treating soil in a radiochemical analysis for strontium.

Acid Processing. Triturate the air-dry soil and pass it through a sieve with an opening diameter of 1 mm. Next take an average sample with a mass of 0.5-1 kg (if the strontium content is increased, the mass of the sample may be reduced) and dry it in the drying cupboard at 105-110 °C during 6-12 h. Weigh the vegetative part of the sample (roots, stems of plants, etc.) and incinerate it in the muffle furnace at 400-500 °C.

Add about 300 mg of a strontium carrier (in the form of a strontium chloride solution) to the combined sample (soil and ash), and then gradually add, in parts, 250 ml of 12 *N* hydrochloric acid. Stir the mixture for 30 min, next filter off the hydrochloric acid extract through two medium-size

* The method does not yield good results when analysing sea water owing to its too low radioactivity and large salt content. In this case perform concentration by precipitating the alkaline (when analysing for cesium) or alkaline-earth (when analysing for strontium) cations with carriers. Strontium is usually coprecipitated in the form of carbonates, and cesium in the form of the ferrocyanide or phosphomolybdate.

pore filter paper in the Büchner filter. Wash the residue with ~500 ml of hot distilled water and again treat it with 500 ml of 6 *M* hydrochloric acid and hot water. Combine the washing water with the hydrochloric acid extracts. Perform the required operations in the solution for separating the radioactive isotopes and recovering the strontium (see below).

Alkaline Melting. Multifold leaching yields satisfactory results in radiochemical analysis not only for strontium, but also for other radioactive isotopes. The "classical" method of melting a weighed sample of the soil with carbonates and alkalis is more time-consuming, but has advantages because the radioactive isotopes of Cs and Ru can be separated in the process of preliminary treatment.

Place a finely triturated weighed sample of the soil in a nickel crucible, add solutions containing carriers of Sr, Cs, Ce, Ru, and evaporate the contents of the crucible until dry under a lamp for evaporation. Next add to the crucible a mixture of KOH, KNO₃, and K₂CO₃ (in the proportion 2 : 1 : 1) in a 5-10-fold amount relative to the mass of the soil sample and roast the material in the muffle furnace at 500 °C for 2 h, rotating the crucible every 15-20 min. Upon melting, the silicic acid passes over into a soluble form, while the ruthenium is oxidized with the formation of soluble ruthenium. Cool the melt and leach it out twice with 10-15 ml of hot distilled water. The Cs and Ru dissolve, while the Sr, Ce, and other isotopes remain in the melt in the form of insoluble carbonates and hydroxides. Treat the melt after cooling it with hydrochloric acid.

Biological Objects. In the radiochemical analysis of various vegetative and animal matter, the sample being analysed is first transformed into "dry" or "wet" ashes.

Dry Ash Formation. First carefully transform a weighed sample of the dried matter at 200 °C, and then roast it at 450-500 °C (at a higher temperature, the Cs begins to volatilize appreciably). Next dissolve the ashes obtained in concentrated hydrochloric or nitric acid. When analysing for strontium, it is better to use nitric acid because in a nitric acid solution strontium nitrate can be precipitated directly by adding fuming HNO₃ (with a density of 1.5 g/cm³).

Wash the dry residue several times with hot distilled water and then heat it for 30 min with a 50% solution of

Na_2CO_3 . Filter off the precipitate, wash it with hot water, dissolve in concentrated HCl , and combine the solution with the main filtrate. The treatment with the carbonate is especially necessary when the matter being investigated contains a large amount of sulphates.

Dry ash formation is simpler, and therefore it is a more general method of treating biological matter, but it may be associated with the loss of volatile components of the object (Cs, P).

Wet Ash Formation. Treat a weighed sample of air-dry matter with concentrated nitric acid; when foaming stops, carefully heat the mixture. After clarification of the liquid, cool the mixture and add a small volume of an oxidizing agent (concentrated sulphuric acid or 30% H_2O_2). Repeat the alternating treatment with nitric acid and the oxidizing agent several times until a transparent solution is obtained (a precipitate of silicic acid remains on the bottom of the vessel).

Radioactive Precipitations. The preparation of samples of radioactive precipitations for analysis consists in methods similar to those described above. When preparing "wet" (rain, snow) samples, use evaporation of the acidified solution in the presence of the relevant carriers or sorption on ion-exchange resins. The treatment of the dry residue after evaporation is different depending on the radioactive element being determined.

To analyse for many elements, among other methods, it is recommended to consecutively treat the finely ground dry residue with a mixture of hydrochloric and nitric acids (3 : 1).

Add carriers containing Sr, Cs, etc., 125 ml of concentrated hydrochloric acid, 50 ml of concentrated nitric acid, and 125 ml of water to the dry residue. Heat the mixture on a water bath, next dry it at 105-110 °C for one hour, add 250 ml of dilute (1 : 1) hydrochloric acid to the residue, heat the solution in the drying cupboard for one hour, and add 250 ml of 0.5 *N* hydrochloric acid to it. Heat on a water bath for 40-50 min and centrifuge.

To transform silicic acid to H_2SiF_6 , treat the precipitate in a platinum utensil with a mixture of sulphuric and hydrofluoric acids. Dissolve the residue in dilute hydrochloric acid. Use the hydrochloric acid extract obtained for analysis.

B. SEPARATION AND DETERMINATION OF RADIOACTIVE Sr

The method consists in the quantitative precipitation of Ca and Sr from a solution in the form of oxalates at $\text{pH} = 4$ with the following roasting of the oxalates to the corresponding oxides, dissolving of the oxides in a dilute acid, removal of Fe^{3+} and Al^{3+} (precipitation of their hydroxides from a hot acid solution), precipitation of alkaline-earth element carbonates, and separation of the Sr^{2+} from the Ca^{2+} by the precipitation of $\text{Sr}(\text{NO}_3)_2$ with fuming nitric acid.

Use two-fold reprecipitation of barium chromate for purifying the Sr^{2+} from Ba^{2+} . Perform radiochemical determination of the strontium according to the activity of the daughter yttrium. Since it is customary practice to express the activity of ^{90}Sr in "strontium units", also determine the content of inactive calcium and strontium in the substance being studied.

Equipment and Reagents

Equipment and Utensils. A counter for measuring activity. A muffle furnace. A centrifuge. Porcelain or quartz crucibles. Glass beakers for 4 and 1 litre. A quartz bowl. Centrifuge tubes for 200 and 40 ml.

Radioactive Substances. Samples for analysis.

Reagents. Acetic and oxalic acids. $(\text{NH}_4)_2\text{CO}_3$. Methanol. Solutions: concentrated, 6-8 M , and 3-5 M HNO_3 ; 8% 17 and 6 M NH_4OH free of CO_2 ; 50% and 3 M $\text{CH}_3\text{COONH}_4$; 1.5 M Na_2CrO_4 ; 30% H_2O_2 .

Performance of Work

Add 100 g of $\text{H}_2\text{C}_2\text{O}_4$ and 25 ml of a 50% solution of $\text{CH}_3\text{COONH}_4$ to the hydrochloric acid solution containing Sr^{2+} , Ca^{2+} , and impurities of other elements obtained as a result of decomposition of a weighed sample of the material being investigated. Heat the mixture to dissolve the oxalic acid, and, by adding ammonium hydroxide, neutralize the solution to a pH of 4 (according to indicator paper). SrC_2O_4 and CaC_2O_4 precipitate. Let the solution with the precipitate stand in a warm spot for four hours. Next filter off the liquid. Dissolve the precipitate of oxalates in 6-8 M nitric acid, add water (approximately to one litre) and 50 g of $\text{H}_2\text{C}_2\text{O}_4$; next bring the pH of the solution up to 4. Separate the newly formed precipitate, transfer it into a quartz

bowl, dry it in a drying cupboard and roast in the muffle furnace at 700-800 °C during 30 min.

Cool the precipitate to room temperature, add 50-60 ml of water, and then dissolve it in 16 *M* nitric acid. Boil the solution to remove CO₂, dilute it to 200 ml, and add ammonium hydroxide (while still hot) to precipitate iron and aluminium.

Filter the solution with the precipitate through a paper filter and wash the precipitate with water.

Add solid (NH₄)₂CO₃ to the filtrate until precipitation of SrCO₃ and CaCO₃ terminates. Separate the carbonates by filtration through a paper filter, dry and weigh them. This mass determines the total content of strontium and calcium carbonates in the material.

Dissolve the carbonates in a minimum amount of 3.5 *M* nitric acid. Place 50-ml portions of the solution into the 200-ml centrifuge tubes and add 120 ml of fuming nitric acid to each of the tubes with constant stirring. Cool the nitrate precipitates with running water while constantly stirring, separate them by centrifuging, and remove the acid.

Add 40 ml of water to each centrifuge tube, dissolve the precipitate, and then add 90 ml of fuming nitric acid. Cool with water, centrifuge, and remove the acid, i.e. repeat the preceding operation.

Transfer the precipitates into a 40-ml centrifuge tube, using 10-20 ml of water for this purpose. Add 1 ml of a solution of a barium carrier and one drop of an indicator (methyl red).

Neutralize the surplus of the acid with a 6 *M* solution of NH₄OH and add 1 ml of 6 *M* acetic acid and 2 ml of a 3 *M* solution of CH₃COONH₄. Dilute the solution to 30 ml and heat it on a water bath. Add 2 ml of a 1.5 *M* solution of Na₂CrO₄ and heat another 5 min. Separate the solution by centrifuging and filter it through a paper filter into a second centrifuge tube.

Heat the second tube on the water bath, add 1 ml of the barium carrier, rapidly stir, and heat for another five minutes.

Separate the solution by centrifuging, and filter it into a third tube. Discard both precipitates. Alkalize the solution with a 17 *M* solution of NH₄OH, add solid (NH₄)₂CO₃ and heat it to coagulate the carbonate precipitate.

Separate the precipitate by centrifuging, and discard the solution.

Dissolve the precipitate in dilute nitric acid, add 1 drop of hydrogen peroxide and 1 ml of a solution of an iron carrier. Heat while stirring to remove CO_2 . Dilute to 15-20 ml and alkalize the solution with ammonium hydroxide free of CO_3^{2-} ions. Heat and stir up to complete precipitation. Separate the precipitate by centrifuging and discard it. Transfer the solution into another 40-ml tube.

Acidify the solution with 6 *M* nitric acid and add 1 ml of an yttrium carrier. Close the tube and store it at least 14 days. After this, alkalize the solution with ammonium hydroxide free of CO_3^{2-} ions and heat it on a water bath for coagulation of the precipitate. Separate the latter by centrifuging and transfer the clear solution into a second tube.

Dissolve the precipitate in 6 *M* nitric acid, dilute the solution up to 10-15 ml, and again form a precipitate with the aid of NH_4OH .

Centrifuge and add the solution to the preceding clear solution. Note the time of the first precipitation.

Again dissolve the precipitate in a minimum amount of 6 *M* nitric acid and add 20 ml of an 8% solution of $\text{H}_2\text{C}_2\text{O}_4$. Heat on a water bath 10-15 min to obtain a precipitate with coarser grains. Cool the mixture and filter it through a dense filter (Whatman 42), wash it three times with methanol in a Büchner filter and transfer it together with the paper substrate onto the target for measurements. Perform the measurement immediately.

Precipitate strontium in the form of the carbonate from the combined solutions after centrifuging by adding $(\text{NH}_4)_2\text{CO}_3$ and heating on a water bath. Cool and filter the solution through a weighed sintered glass filter (No. 4). Wash the precipitate with water and methanol, dry it in a drying cupboard at 110 °C, weigh and calculate the amount of strontium.

After measuring the activity of the source of Y, separate the paper with the substance from the material of the target, transfer it into the weighed crucible, incinerate it, roast at 800-900 °C, and weigh in the form of Y_2O_3 .

Evaluate the amount of separated yttrium. To obtain the yields of yttrium and strontium, correct the result of measuring the activity of the yttrium to the zero time.

C. SIMULTANEOUS DETERMINATION OF RADIOACTIVE ^{106}Ru , ^{137}Cs , ^{144}Ce , AND ^{90}Sr * IN NATURAL OBJECTS

It is often necessary to determine simultaneously the content of several radioactive isotopes from one weighed sample of a natural material. The literature describes many such schemes including modern methods of chemical analysis: coprecipitation, extraction, ion exchange, etc. One of the schemes for separating ^{90}Sr , ^{137}Cs , and ^{144}Ce is given below (Fig. 17.11).

Equipment and Reagents

Equipment and Utensils. A muffle furnace. A centrifuge. A desiccator. A lamp for evaporation. Chromatographic columns. Nickel crucibles. Separatory funnels for 1.0, 0.5, and 0.2 litre. Beakers for 1.0 and 0.5 litre.

Reagents. Cation exchanger KU-2 or Dowex-50. Phenolformaldehyde cation exchanger (type Dualite S-3). NH_3 . KOH . KNO_3 . K_2CO_3 . Na_2CO_3 . KIO_4 . LiOH . CCl_4 . Solutions: 0.2 N SrCl_2 , CsCl , CeCl_3 , RuCl_3 or $\text{Sr}(\text{NO}_3)_3$, CsNO_3 , $\text{Ce}(\text{NO}_3)_3$ and $\text{Ru}(\text{NO}_3)_3$; 0.5 M LiOH ; 0.2 M LiCl ; 6 M , 0.2 and 0.1 N HCl ; 9 M H_2SO_4 ; concentrated (with a density of 1.5 g/cm^3) HNO_3 ; concentrated NH_4OH ; 30% H_2O_2 .

Performance of Work

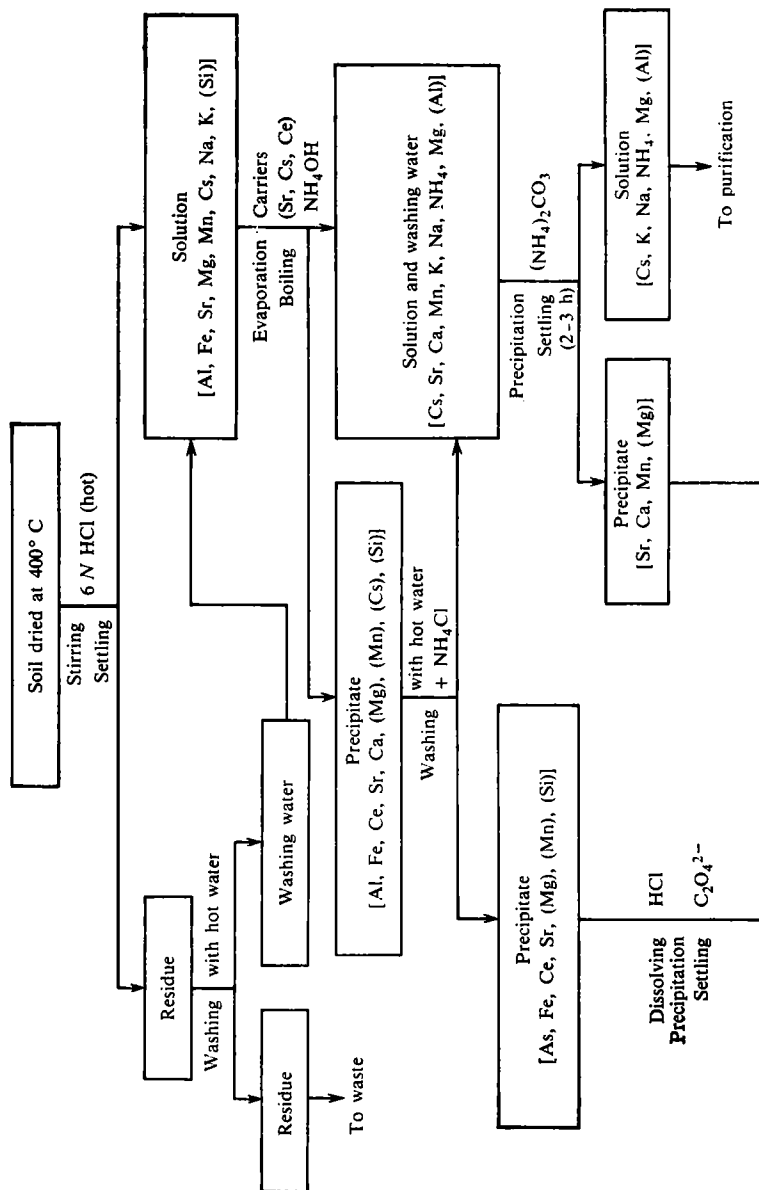
Prepare the specimen preliminarily by the method of alkaline melting**.

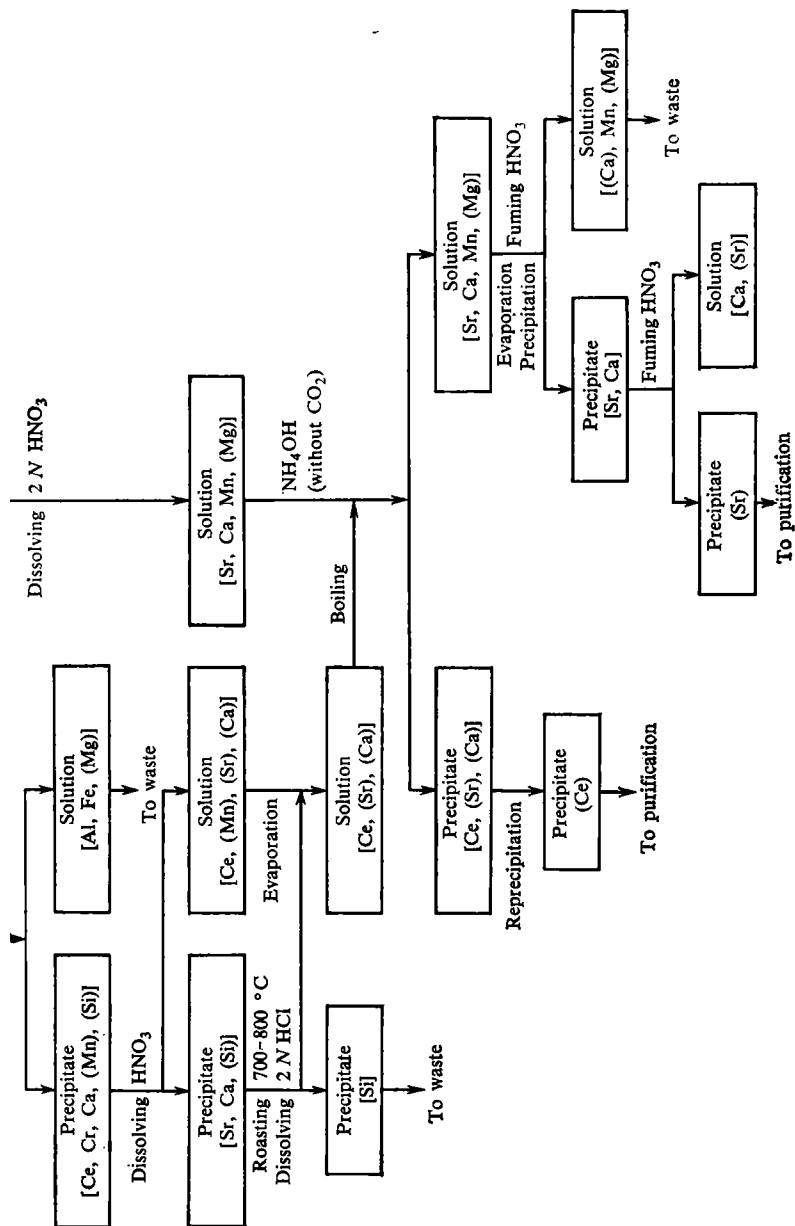
(a) Determination of ^{106}Ru

Add 0.25 g of KIO_4 (for oxidizing the ruthenium to the tetroxide) to the solution obtained after processing the alkaline melt with hot water. Separate the precipitate by

* The listed isotopes, as well as ^{147}Pm (separated according to the given procedure together with ^{144}Ce) are the basic long-lived products of fission of uranium ($\sim 98\%$ in the composition of fragments three years old).

** When there is a large content of anions in the specimen (phosphates, etc.), after melting and leaching out adsorb the cations from a 0.1 N solution of acid on the cation exchanger KU-2 or Dowex-50, wash out the anions with water, and then desorb the cations with 6 M hydrochloric acid. If it is necessary to analyse the specimen for its content of ^{32}P and ^{35}S , this procedure can be a convenient method for the preliminary separation of the anions and cations.





centrifuging (zirconium separates). Neutralize the solution with 9 *M* sulphuric acid to a pH of about 7. After adding 10 ml of distilled carbon tetrachloride, gradually lower the pH of the solution to 4, adding dropwise 9 *M* sulphuric acid. Separate the layers and extract the ruthenium from the CCl_4 with 6 *M* hydrochloric acid.

(b) Determination of ^{137}Cs

Treat the aqueous layer after the extraction of ruthenium with a concentrated solution of LiOH and remove the formed precipitate of Li_2CO_3 by centrifuging. Fill a chromatographic column with the cation exchanger Dualite S-3, transfer the resin into the Li^+ form, washing it with 100 ml of a solution of LiCl and then with 50 ml of water. Pass the solution containing radioactive cesium through the column and then wash the resin with 50 ml of water. Again treat the column with 125 ml of a 0.5 *N* solution of LiOH (for elution of the potassium). Pass 50 ml of water through it and elute the lithium with 125 ml of 0.2 *N* hydrochloric acid. Extract the cesium finally with 50 ml of 6 *M* hydrochloric acid.

Maintain the rate of passing the solution through the resin at 2-3 ml/min in all cases.

(c) Determination of ^{144}Ce

Treat the solid residue of the alkaline melt while heating it with 10 ml of nitric acid. Evaporate the solution two times until dry, adding each time several millilitres of concentrated nitric acid for dehydration of the silicic acid. Treat the dry residue with 5 ml of 6 *M* hydrochloric acid and 2-3 drops of 30% hydrogen peroxide for reducing the cerium. Centrifuge the silicon dioxide precipitate and discard it. Dilute the clear solution up to 10 ml and neutralize it with gaseous ammonia; cerium hydroxide precipitates. Reprecipitate the cerium in the form of the oxalate.

(d) Determination of ^{90}Sr

After removing the cerium in the form of its hydroxide from the solution, precipitate strontium (by adding Na_2CO_3). Dissolve the precipitate in 6 *N* nitric acid and purify the

strontium by twofold reprecipitation with fuming nitric acid. Remove the traces of calcium by leaching out the solid nitrate with an alcohol-ether mixture.

**Experiment 17.11. DETERMINATION OF
A HEAVY COMPONENT ACCORDING TO THE EFFECT
OF BACKWARD SCATTERING OF β -RAYS [2]**

The intensity of β -radiation reflected from a specimen depends on the charge Z of the nuclei. This relation can be expressed approximately by the empirical equation

$$\Delta = K_a Z^{2/3}$$

where Δ is the reflection coefficient equal to the ratio of the reflected radiation to the flux of radiation incident on the specimen, and K_a is a proportionality factor.

The maximum energy of the reflected radiation E_{refl} is related to the maximum energy of the incident radiation E_{inc} by the empirical expression

$$E_{\text{refl}} = 0.127Z \times 0.38E_{\text{inc}}$$

The larger the atomic number of an element, the greater are the flux and energy of the reflected radiation. These properties make it possible to determine the content of a heavy element in the presence of lighter ones.

Ores are a suitable object for such an analysis. Indeed, in iron ore, iron has the largest atomic number in comparison with the remaining components (O, Si, Al), which makes it possible to determine its content. The method was also used for determining the content of tungsten in steel and the ash content of coals.

Any of the indicated systems can be used for performing the work. The accuracy of analysis can be improved substantially by introducing an absorber in the path of the reflected radiation (between the specimen and the registering instrument).

Equipment and Reagents

Equipment. A counter with a detector of β -radiation (a Geiger-Müller counter, an ionization chamber, or a scintillation crystal) adapted for the registration of reflected radiation. A set of aluminium ab-

sorbers (50, 100, 150, and 200 mg/cm²). A set of containers for powdered specimens (the latter must have a grain size of about 0.07 mm).

Radioactive Substances. A source of β -radiation (³²P, ²⁰⁴Tl, ¹⁸⁵W, ⁴⁵Ca) with an activity of 37-370 MBq (1-10 mCi) (depending on the kind of registering instrument). Closed sources (²⁰⁴Tl, ⁹⁰Sr, ⁹⁰Y) with an activity of ~ 200 MBq (~ 5 mCi).

Reagents. A set of specimens with a known content of the heavy component for plotting a calibration curve. A set of specimens with an unknown content of the heavy component.

Performance of Work

Measure the intensity of the reflected radiation for the series of specimens with the known content of the heavy component.

Use the data obtained to plot a calibration graph of the activity against the content of the element being analysed in a specimen.

Measure the flux of the reflected radiation of the specimens with an unknown content of the element being analysed.

Find the content of the heavy element according to the calibration graph.

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Chapter 18 Use of Radioactive Isotopes for Determining Physicochemical Constants [1-3]

The features of radioactive methods of investigation—the high sensitivity of determining negligibly small amounts and the possibility of watching transfer processes—allowed them to be widely used for determining physicochemical constants and studying the kinetics of physicochemical processes. It is general knowledge that the introduction of tracer amounts of radioactive substances at low specific activities does not affect the relevant constants.

On the other hand, the introduction into a substance of isotopes with a high radioactivity leads to a change in the physicochemical properties of substances; the nature of this change can also be used for determining the properties of the substance itself or for investigating a process.

When determining physicochemical constants, it is often necessary to know the exact amount of substance in a sample. The use of radioactive tracers for determining physicochemical constants allows one to replace the conventional chemical operations of determining the mass of a substance with measurement of its radioactivity. Owing to the identity of the chemical properties of isotopes, the specific activity S of a labelled compound (calculated for the element) remains constant in ordinary chemical operations. If a certain part of a compound having the activity I_x is separated, the mass m_x corresponding to it is determined by the relation

$$m_x = I_x/S \quad (18.1)$$

The general advantages of the method of radioactive tracers include:

- the universal nature of the method due to the availability of radioactive isotopes for all the elements of the periodic table;

- the absence in the majority of cases of the influence of elements having close properties;

the possibility of performing measurements in the presence of foreign agents (acids, salts, volatile and readily decomposed substances, organic components. etc.);

the simplicity and rapidity of performing the main operations of activity measurement, and the possibility of their automation in large-scale determinations.

Experiment 18.1. DETERMINATION OF SOLUBILITY OF SPARINGLY SOLUBLE SUBSTANCES [4, 5]

One of the characteristics of a solid is its solubility in water or another solvent. The solubility is usually expressed by the number of moles of the solute in one litre of a saturated solution at the given temperature.

To determine the solubility by the method of radioactive tracers, it is necessary to: calculate the minimum specific activity of the compound being studied needed to perform measurements; prepare a compound containing a radioactive isotope and determine its specific activity S (in cpm/ml); prepare a solution of the compound that is saturated at the given temperature and measure the activity I_s of a sample of the solution having the volume V_s .

The experimental data are used to calculate the solubility L of the substance (in mol/litre) by the formula

$$L = \frac{I_s \times 1000}{V_s S} \quad (18.2)$$

where L is the solubility, I_s is the activity of a sample of the saturated solution, cpm, V_s is its volume, ml, and S is the specific activity of the labelled compound, cpm/mol.

A. SCHEME OF RUNNING THE EXPERIMENT

(a) Appraisal of the Required Specific Activity

The quantity I_s/V_s being measured depends on the specific activity S of the compound being studied and is the smaller, the lower is the solubility of the compound. Consequently, to ensure a sufficient accuracy of measurement, it is necessary, at least tentatively, to know the solubility of the compound. It is usually found proceeding from the properties

of the compound being investigated or from preliminary determinations.

It is desirable that the activity I_s of the solution sample being measured be several times larger than that of the background. For example, at a background value of 50 cpm and a volume of the saturated solution sample of 0.5 ml, the measured activity I_s must be at least 500 cpm. This condition will be observed if

$$S \geq \frac{I_s \times 1000}{V_s L} \quad (18.3)$$

In our example, we have

$$S = \frac{500 \times 1000}{0.5 L} = \frac{10^6}{L}$$

i.e. for compounds whose solubility is 10^{-4} mol/litre, the specific activity must be at least 10^{10} cpm/mol.

(b) Preparation of a Substance Labelled with Respect to a Given Element and Determination of Its Specific Activity

The direct determination of the specific activity of a labelled sparingly soluble compound is associated with a large experimental error. It is therefore good practice to determine the specific activity S_1 of a soluble compound used to prepare a precipitate of the poorly soluble salt with the specific activity S_s (calculated for the element). Obviously, when calculating for the element, we have

$$S_1 = S_s = S$$

The value of S is determined by the ratio of the introduced activity I of the isotope to the total mass of the labelled element:

$$S = \frac{I}{m_1 + m_0} \quad (18.4)$$

where m_1 is the mass of the element introduced with the soluble salt, and m_0 is the mass of the same element introduced together with the radioactive solution.

The overall accuracy of determining the solubility depends first of all on the accuracy of determining the specific activity, which must be performed especially thoroughly. The great-

est error is associated with the determination of the value of I .

All substances whose activity is to be measured must be prepared in the same way, have the same thickness, must not differ greatly in their activity, and the latter, in turn, must be measured in identical conditions. To avoid the errors associated with the determination of large values of the activity of the initial solution I_0 , several consecutive dilutions are performed until the activity of the preparation for measuring I' becomes about the same as the activity of a sample of the saturated solution. The required dilution multiplicity factor n' is appraised according to the certificate of the isotope proceeding from the value of the registered volume specific activity S' and the volume of the sample V' used for measurement:

$$n' = \frac{S'V'}{I'}$$

Dilution of the initial solution is performed consecutively with several portions of the solvent, choosing the volumes in accordance with the available pipettes and flasks.

The accurate value of the registered specific activity S' is determined on the basis of measuring the activity of a sample of the dilute solution with account taken of the dilution multiplicity factor n' :

$$S' = \frac{I'}{V'} n'$$

Further, assuming that m moles of the labelled compound have to be prepared for the experiment, one must calculate V_0 —the volume of the initial solution of the isotope that is needed to ensure the calculated value of the specific activity S . For example, if $S = 1 \times 10^{10}$ cpm/mol, $m = 2 \times 10^{-3}$ mol, and $S' = 2 \times 10^8$ cpm/ml, the required volume of the initial solution is

$$V_0 = \frac{Sm}{S'} = \frac{10^{10} \times 2 \times 10^{-3}}{2 \times 10^8} = 0.1 \text{ ml}$$

The mass of the carrier $m = m_1 + m_0$ introduced when preparing a compound labelled with a given isotope is calculated on the basis of a titre of the solution used and the certificate of the isotope. After having taken the corresponding volume of the titrated solution and added the solution of the isotope, one precipitates the compound with its anion or

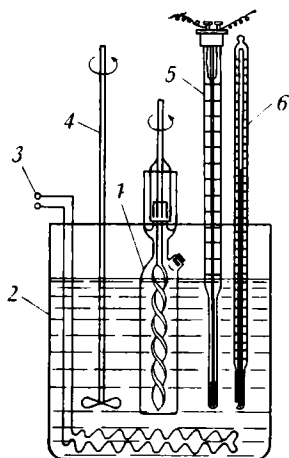


Fig. 18.1. Arrangement for determining solubility:
 1—glass vessel with water seal and stirrer; 2—thermostat
 3—heater; 4—stirrer; 5—contact thermometer; 6—thermo-
 meter

cation labelled using a suitable precipitant. The precipitate with the specific activity S is used to determine the solubility.

A solution of the labelled compound saturated at the given temperature is obtained. For this purpose, it is mixed with a solvent in an arrangement for determining the solubility (Fig. 18.1) or by shaking in closed vessels until equilibrium is reached, which is established by taking samples of the solution in definite intervals of time.

All preparations for measuring the activity are produced in identical conditions by evaporating a definite volume of the solution in standard bowls. If volatile compounds may form or if the volumes to be evaporated are very large, the method of precipitation with carriers is used. All activity measurements are also performed in identical conditions. The time interval between activity measurements must be small in comparison with the half-life of the isotope, otherwise a correction for decay must be introduced. An equilibrium value at the given temperature that is used to calculate the solubility of a compound by formula (18.2) corresponds to the constant value of the volume specific activity of the saturated solution samples.

B. DETERMINATION OF SOLUBILITY OF SrSO_4 IN WATER

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. A device for shaking or an arrangement for determining solubility (see Fig. 18.1). A centrifuge with tubes. A lamp for evaporation. A planchet. Test tubes with ground-glass joints for 10 ml (6). Beakers for 100 ml (2). A micropipette with a syringe. Pipettes for 5 or 15 ml. Burettes for 25 ml (2). Measuring flasks for 100 ml (2). Glass bowls for measuring activity or test tubes for a scintillation counter with a well.

Radioactive Substances. A solution of SrCl_2 containing ^{89}Sr with a specific activity of 3.7 MBq (0.1 mCi/ml).

Reagents. 0.05 *M* solutions of $\text{Sr}(\text{NO}_3)_2$ and MgSO_4 .

Performance of Work

Calculate the specific activity S of the labelled strontium sulphate needed for determining the solubility by assuming that $L = 5 \times 10^{-4}$ mol/litre and that a sample of 0.2 ml of a saturated solution should provide a counting rate of 500 cpm. According to the certificate of the radioactive isotope, calculate the volume specific activity S' of the initial solution of $^{89}\text{SrCl}_2$ needed for preparing the labelled compound, and the multiplicity of its dilution for its determination so that 0.2 ml of a sample of the saturated solution would provide a counting rate of ~ 500 cpm. Using the micropipette and the measuring flasks, dilute the solution until the required multiplicity of dilution is obtained.

To determine the volume specific activity of the dilute solution, take two 0.5-ml samples into glass bowls for measuring the activity, evaporate the solution under the lamp until dry. First determine the activity of the preparation I' by measuring it twice (performing each measurement during one minute). More accurate measurement can be performed later together with the other preparations. By multiplying the ratio I'/V' by the dilution multiplicity factor, obtain the value of S' and compare it with what was calculated according to the data in the certificate.

Prepare labelled SrSO_4 as follows. Introduce 10 ml of a 0.05 *M* solution of $\text{Sr}(\text{NO}_3)_2$ into a 100-ml beaker with a pipette. Add the active solution containing ^{89}Sr in the previously calculated volume V_0 needed to form the required specific activity. Carefully, without splashing and evapora-

tion, heat the solution to about 60 °C and precipitate SrSO_4 by slowly adding 10-12 ml of a 0.05 *M* solution of MgSO_4 . Centrifuge the solution and repeatedly wash the precipitate with water.

Divide the moist precipitate into two halves without weighing, place the portions into glass test tubes with ground-glass joints, and add 10 ml of distilled water to each portion. Place the vessels during 10-15 min into a water bath with a temperature of 50-60 °C to supersaturate the solution, then put them into a thermostatted shaker (25 °C) or into an arrangement for determining the solubility. Every 30 min take 0.2-ml samples of the clear solution into the bowls for measuring the activity. Evaporate the solutions in the bowls, and measure the activity of the samples. Continue to take samples until a constant value of the activity is reached. Choose the duration of measurement so that the relative statistical deviation does not exceed 3% at a confidence level of 0.95. Plot the activity against the duration of stirring and find the mean value of the activity corresponding to the concentration of a saturated solution.

Calculate the solubility of SrSO_4 in water at the temperature of the experiment, and also the solubility product. Appraise the error of the method. Compare the obtained value of the solubility with tabulated data and determine whether the revealed deviations are significant.

C. DETERMINATION OF SOLUBILITY OF PbI_2 IN WATER AND IN NaI SOLUTIONS

Equipment and Reagents

Equipment and Utensils. A counter with a scintillation detector having a well. A shaker. A lamp for evaporation. A centrifuge. A planchet. Test tubes with a ground-glass joint (6). A flask for 50 ml. A burette for 25 ml. A micropipette for 1 ml. A beaker for 100 ml.

Radioactive Substances. A solution of NaI containing ^{131}I with a specific activity of $\sim 10^7$ cpm/ml.

Reagents. Solutions: titrated 0.01, 0.05, 0.1 *M*, 0.2 *M* NaI ; 0.2 *M*, $\text{Pb}(\text{CH}_3\text{COO})_2$; 0.05 *M* AgNO_3 ; 5% Na_2SO_3 (freshly prepared). Na_2SO_3 (crystalline).

Performance of Work

Determine the volume specific activity of the initial solution *S* after the corresponding dilution as described in Sec. B.

Different ways can be used to determine the activity of ^{131}I being registered:

1. Take samples of the solution into test tubes for measuring the activity by means of a scintillation transducer with a well.

2. Take samples of the solution into bowls for measuring the activity, add a few minute crystals of Na_2SO_3 , and carefully evaporate the solutions, protecting them from the action of light.

3. Take samples of the solution in the beaker with 20 ml of water, add a few drops of a 5% solution of Na_2SO_3 , 5 ml of a 0.1 *M* solution of NaI as a carrier, heat the solutions to 70 °C, and precipitate the iodine in the form of silver iodide, slowly adding 20 ml of a 0.05 *M* solution of AgNO_3 . Filter off the precipitate of Ag^{131}I in a sectional funnel for filtration, wash it a little, and dry it under the lamp. Cover the filter with varnish, and measure the activity of the preparation with a β -counter.

Prepare all the specimens for measuring the activity to be registered in the same way and retain identical conditions of the measurements. Calculate the required value of the specific activity of the iodide proceeding from a solubility of PbI_2 equal to $\sim 10^{-3}$ mol/litre.

Calculate the volume V_0 of the initial solution of Na^{131}I that has to be added to obtain 1.5×10^{-3} mol of lead iodide labelled with ^{131}I . To prepare $\text{Pb}^{131}\text{I}_2$, add from a burette 15 ml of a 0.2 *M* solution of NaI and the calculated volume V_0 of the active solution into the 100-ml beaker. Heat the solution slightly, and precipitate $\text{Pb}^{131}\text{I}_2$ by adding 10 ml of a 0.2 *M* solution of $\text{Pb}(\text{CH}_3\text{COO})_2$ (perform precipitation using a surplus of the precipitant). Let the precipitate settle, after which separate it by centrifuging and wash it several times with water.

Calculate the specific activity of the precipitate by formula (18.4). Determine the solubility of the lead iodide in water (test tube No. 1) and in solutions of NaI —0.01, 0.05, and 0.1 *M* (tubes No. 2, 3, and 4, respectively). For this purpose, distribute the precipitate between four numbered test tubes and add to each of them 10 ml of the corresponding solvent. Close the tubes with ground-glass stoppers, place them into the thermostatted shaker, and stir them during two hours at 20–25 °C. Next take 1 ml for a sample from each tube and determine the activity of the saturated solu-

tion. Calculate the value of the solubility of PbI_2 in each solution. Plot a curve of the solubility against the concentration of the NaI in the solution.

D. DETERMINATION OF SOLUBILITY OF A SPARINGLY SOLUBLE SALT FOR VARIOUS pH's OF THE SOLUTION

Equipment and Reagents

Equipment and Utensils. A counter for measuring β -radiation. A thermostat with vessels for determining the solubility (see Fig. 18.1). A centrifuge, a pH meter. A water bath. A lamp for evaporation. A planchet. Glass or aluminium bowls for measuring activity (6). Measuring flasks for 25 and 100 ml. Pipettes for 1 and 10 ml with syringes.

Radioactive Substances. A solution ($10^{-4} M$) of $\text{Sr}(\text{NO}_3)_2$ containing ^{89}Sr with a specific activity of 3.7 MBq/ml (0.1 mCi/ml). A solution ($10^{-4} M$) of CaCl_2 containing ^{45}Ca with a specific activity of 3.7 MBq/ml (0.1 mCi/ml).

Reagents. A universal indicator. Solutions: 0.1 M SrCl_2 ; 0.1 M CaCl_2 ; 0.1 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$; 0.1 M Na_2HPO_4 ; 0.01, 0.05; 0.10; 0.15 and 0.20 N HCl ; 0.01 N NH_4OH .

Performance of Work

(a) Determining the Solubility of SrC_2O_4

Calculate the activity of $^{89}\text{SrCl}_2$ needed to determine the solubility of SrC_2O_4 and the volume V_0 of a $10^{-4} M$ solution of $^{89}\text{Sr}(\text{NO}_3)_2$ with a specific activity of 3.7 MBq/ml (0.1 mCi/ml) that must be added to 20 ml of a 0.1 M solution of $\text{Sr}(\text{NO}_3)_2$, provisionally assuming the solubility of strontium oxalate in a neutral medium to be 10^{-4} mol/litre, and also proceeding from the fact that the volume specific activity of a saturated solution should be 1000 cpm/ml.

Add the calculated amount of the active solution in the 25-ml measuring flask to the solution of $\text{Sr}(\text{NO}_3)_2$ and add water to bring the solution up to the mark. Determine its specific activity. For this purpose, use a pipette (preliminarily washed with the solution being analysed) to take 1 ml of the solution into the 100-ml measuring flask and bring the volume up to the mark with an acidified aqueous solution, put 1 ml of the solution into a glass bowl, dry it under the lamp and measure the activity of the dry residue. Cal-

culate the specific activity of the strontium (in cpm/mg) by formula (18.3).

Precipitate SrC_2O_4 from the prepared solution with a small surplus of a 0.1 *M* solution of $(\text{NH}_4)_2\text{C}_2\text{O}_4$. Consolidate the precipitate by heating the mixture on the water bath, separate it by centrifuging, wash it several times with water, divide it into six parts and transfer them into six vessels for determining the solubility. To each precipitate add 20 ml of the relevant solvent—an aqueous solution with a pH varying from 1 to 7. Prepare these solutions by consecutively diluting hydrochloric acid, control the pH with a universal indicator or the pH meter. Stir the precipitates with the solvent during 3 h in the thermostat (25 °C) or at room temperature (see Fig. 18.1).

After equilibrium sets in, again determine the pH of the solutions. Separate the precipitates by centrifuging, and use a pipette (preliminarily washed with the saturated solution obtained) to take samples from the solutions for measuring their activity. Measure the counting rate of the preparations obtained and of those for determining the specific activity simultaneously.

Calculate the solubility of SrC_2O_4 by formula (18.2). Use the data obtained to plot the solubility against the pH of the solution. Explain the nature of the curve.

(b) Determining the Solubility of CaC_2O_4

Use the radioactive isotope ^{45}Ca . Perform this experiment in the same way as the preceding one with the following changes. Determine the solubility of the precipitate in solutions with an HCl concentration from 0.01 to 0.2 *N*. Take an amount of ^{45}Ca for running the experiment so as to obtain a specific activity of ~ 5000 cpm/mg. Plot the solubility against the acidity of the solution. Explain the results of the experiment.

(c) Determining the Solubility of Potassium and Strontium Phosphates

Use the radioactive isotopes ^{45}Ca and ^{89}Sr . Perform the experiment in the same way as the preceding one. Determine the content of the cation in solutions of various acidity with a pH from 2 to 8. Take the amounts of the relevant isotopes

so as to obtain specific activities of $\sim 10\,000$ cpm/mg.

Plot the concentration of the cation against the pH of the solution. Explain the shape of the curve.

E. DETERMINATION OF SOLUBILITY OF MgNH_4PO_4 IN SOLUTIONS OF A MAGNESIAL MIXTURE OF VARIOUS CONCENTRATIONS

M. Neiman proposed a method of determining the solubility of sparingly soluble compounds in the presence of foreign ions with a high concentration. The method makes it possible to choose the optimal amount of the precipitant. An advantage of the method also consists in that there is no need of accurately determining the specific activity of the labelled compound. The experiment and calculations are performed as follows.

Assume that a solution contains a weightless amount of radioactive ions of A with an activity of I_0 (in cpm). We add m mmol of inactive ions of A to it and precipitate the compound B we are interested in by adding the relevant reagents to the solution (V_1 is the volume of the solution, ml). We filter off the precipitate of B containing a part of the activity, wash it, and determine its activity I_1 (in cpm). A part of the active substance gets into the filtrate owing to the solubility of the substance B. We again add m mmol of the carrier A to the filtrate and again precipitate B (V_2 is the volume of the solution, ml). We filter off the precipitate of B, wash it, dry it, and determine its activity I_2 (in cpm).

If the solubility of the compound B being sought is L (in mmol/ml), then after the first precipitation LV_1 mmol of the salt remains in the solution, and $(m - LV_1)$ mmol in the precipitate.

The activity I_1 is only a part of the total activity I_0 :

$$I_1 = I_0 \frac{m - LV_1}{m}$$

After the second precipitation, LV_2 remains in the solution, and $m + LV_1 - LV_2$ mmol in the precipitate. The activity of the second precipitate is also only a part of the general activity I_1 :

$$I_2 = \frac{I_0 LV_1}{m} \cdot \frac{m + LV_1 - LV_2}{m + LV_1}$$

Designating I_1/I_2 by b , we obtain:

$$L = \frac{mV_1b_1 \pm \sqrt{m^2b^2V_1^2 + 4m^2V_1[V_1 + b(V_1 + V_2)]}}{2V_1[V_1 + b(V_1 - V_2)]} \quad (18.5)$$

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. A lamp for evaporation. A planchet. Measuring flasks for 25 and 50 ml (4 each). Beakers for 100 ml (4). Sectional funnels (4). A wash bottle.

Radioactive Substances. A solution (10^{-4} M) of Na_2HPO_4 containing ^{32}P with a specific activity of ~ 1000 cpm/ml.

Reagents. Alcohol (or acetone). Solutions: 1% and dilute (1 : 10) NH_4OH ; 0.2 M MgCl_2 ; 0.5 M NH_4Cl ; 0.1 M Na_2HPO_4 ; 0.2 N HCl ; alcohol—of phenolphthalein.

Performance of Work

Dilute the initial active solution of $\text{Na}_2\text{H}^{32}\text{PO}_4$ to a value of the volume specific activity of ~ 1000 cpm/ml. Perform the experiments at various volumes of the precipitant, keeping the other conditions of precipitation identical. Mix solutions in the following amounts in four 25-ml measuring flasks (No. 1-4):

Number of flask	1	2	3	4
Solutions, ml:				
0.2 N HCl	0.1	0.1	0.1	0.1
$\text{Na}_2\text{H}^{32}\text{PO}_4$ (carrier-free)	1	1	1	1
0.1 M Na_2HPO_4	1	1	1	1
0.2 M MgCl_2	0.5	1.0	2.0	10
0.5 M NH_4Cl	0.4	0.8	1.6	8

Add 2-3 drops of phenolphthalein to each solution, immerse the flasks into water heated to 60-70 °C, and add ammonia dropwise up to a pink colour. Bring the volume of each solution up to 25 ml with water, stir it well, and allow it to settle during one hour at room temperature. Filter the solutions through a dense filter in a sectional funnel into the 50-ml measuring flasks (No. 1'-4'). Wash the precipitates with ammonia water, next with alcohol or acetone, after which dry them under the lamp and coat them with varnish.

Add solutions in the following amounts to the filtrates in the 50-ml measuring flasks (1'-4'):

Number of flask	1'	2'	3'	4'
Solutions, ml:				
0.2 <i>N</i> HCl	0.1	0.1	0.1	0.1
0.1 <i>M</i> Na ₂ HPO ₄	1	1	1	1
0.2 <i>M</i> MgCl ₂	0.5	1.0	2.0	10
0.5 <i>M</i> NH ₄ Cl	0.4	0.8	1.6	8

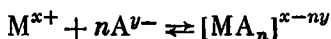
Repeat the precipitation as described above for the first solutions and obtain the relevant precipitates. Bring the volumes of the solutions up to the mark by adding water. Separate the precipitate in a sectional funnel, dry and coat it with varnish. Measure the β -activity of the preparations.

Calculate the solubility of MgNH₄PO₄ in each of the four cases by formula (18.5); plot the multiplicity of the excess precipitant against the solubility.

Choose the optimal conditions for precipitating the phosphate ion by a magnesian mixture (an ammoniacal solution of magnesium and aluminium chlorides).

Experiment 18.2. DETERMINATION OF FORMATION CONSTANTS OF COMPLEX COMPOUNDS BY THE ION-EXCHANGE METHOD [6]

The formation of a complex compound of the type MA_{*n*} from a central ion and a ligand is expressed by the equation



The formation (stability) constant of the complex ion is the basic thermodynamic characteristic of a complex compound and can be determined from experiments involving the distribution of the ions of a metal between two phases, for example between an ion-exchange resin and a solution.

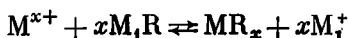
In conditions of a constant ionic strength of the solution, when the ratio of the activity coefficients is a constant quantity, what is called the concentration constant of formation β is evaluated by introducing the concentrations of the relevant ions instead of their thermodynamic activities into the equation expressing the law of mass action:

$$\beta = \frac{[MA_n]^{x-ny}}{[M^{x+}][A^{y-}]^n} \quad (18.6)$$

The method is based on studying the change in the coefficient of distribution of a cation between the resin and the solution in the presence of a complexing agent.

The use of radioactive isotopes in tracer amounts appreciably simplifies calculations because the composition of the solution and of the solid phase does not virtually change. Owing to the negligibly small concentration of the tracer ion, the equilibrium concentration of the ligand can be assumed to equal the initial one. The possibility of directly determining the amount of an element in a solution according to its radioactivity (without preliminary separation) substantially simplifies the calculations and the procedure of running an experiment, and improves the accuracy of the method.

If cation exchange proceeds according to the reversible reaction



the distribution of the tracer between the cation exchanger and the solution is characterized by the distribution coefficient K_{d0} related to the constant K_{ex} of the ion exchange reaction:

$$K_{d0} = \frac{[MR_x]}{[M^{x+}]} = K_{ex} \frac{[M_1R]^x}{[M_1^+]^x} = \text{const} \quad (18.7)$$

In the presence of complexing agent anions A^{y-} capable of forming complex ions of the type MA^{x-y} , MA_2^{x-2y} , etc. with a metal, the conditions of equilibrium of the exchange reaction on the cation exchanger are described by new equations expressing the distribution of the complex ions participating in ion exchange. The concentration of the complex ions in an equilibrium solution is determined by the value of the formation constant β_i (quantities that are reciprocals of the instability constants):

$$\begin{aligned} \beta_1 &= \frac{[MA^{x-y}]}{[M^{x+}][A^{y-}]} & \beta_2 &= \frac{[MA_2^{x-2y}]}{[M^{x+}][A^{y-}]^2} \\ &\dots\dots\dots & & \\ \beta_n &= \frac{[MA_n^{x-ny}]}{[M^{x+}][A^{y-}]^n} \end{aligned} \quad (18.8)$$

In addition, material balance equations can be compiled to express the total concentration of the metal in the solu-

tion c_M and of the cation exchange c_{MR} :

$$c_M = [M^{x+}] + [MA^{x-y}] + [MA_2^{x-2y}] + \dots \\ \dots + [MA^{x-ny}] \quad (18.9)$$

$$c_{MR} = [R_x M] + [R_{x-y} MA] + \dots \quad (18.10)$$

In practice, the determination of the formation constants consists in running the required number of experiments for determining c_M and c_{MR} and solving the resulting system of equations.

A. THE SCHUBERT METHOD

It is the simplest to determine the composition and formation constants of a complex ion if only one complex compound MA^{x-ny} forms in the system that does not participate in the exchange on the cation exchanger. The relevant expressions for the distribution coefficients and formation constants have the form:

$$K_{d0} = \frac{[R_x M]}{c_M} = \frac{[R_x M]}{[M^{x+}]}$$

(it characterizes the distribution in the absence of a complexing agent)

$$K_d = \frac{[R_x M]}{c_M} = \frac{[R_x M]}{[M^{x+}] + [MA^{x-ny}]}$$

(it characterizes distribution in the presence of a complexing agent)

$$\beta = \frac{[MA^{x-ny}]}{[M^{x+}][A^{y-}]^n}$$

(it characterizes the stability of the complex).

By combining these expressions, we obtain the Schubert equation:

$$\beta = \frac{(K_{d0}/K_d) - 1}{[A^{y-}]^n} \quad (18.11)$$

When processing experimental data, it is convenient to use an expression obtained by taking logarithms:

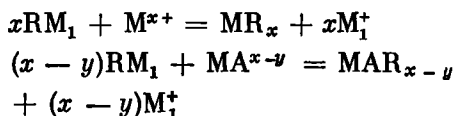
$$\log \left(\frac{K_{d0}}{K_d} - 1 \right) = \log \beta + n \log [A^{y-}] \quad (18.12)$$

A straight line is plotted in the coordinates $\log [(K_{d0}/K_d) - 1]$ against $[A^{\nu-}]$ whose slope corresponds to n , and whose ordinate intercept equals $\log \beta$.

B. THE FRONEUS METHOD

When several complex ions of the type $[M^{x+}A_n]^{x-n\nu}$ are present in a solution and several complex ions having a positive charge participate in exchange with the cation exchanger, it is good to use a general method proposed by Froneus for determining the composition and stability of complex forms.

The corresponding equations of exchange and complex formation are as follows:



The following expressions for the distribution coefficients

$$\begin{aligned} \frac{[MR_x]}{[M^{x+}]} &= K_{d0} \\ \frac{[MAR_{x-y}]}{[MA^{x-y}]} &= K_{d1} \end{aligned}$$

and for the material balance:

$$c_M = K_{d0} [M^{x+}] + K_{d1} [MA^{x-y}] + \dots \quad (18.13)$$

correspond to these equations.

If we assume that the metal is in the $+2$ oxidation state, while the ligand is singly charged, the equations for the coefficients of distribution of the metal K_d between the solution and the resin will be

$$K_d = \frac{c_{MR}}{c_M} = \frac{K_{d0} [M^{2+}] + K_{d1} [MA^+]}{[M^{2+}] X} \quad (18.14)$$

where $X = 1 + \sum_{j=1}^N \beta_j [A]^j$.

Assuming that $l = K_{d1} \beta_1 / K_{d0}$, we obtain the equation

$$K_d = \frac{K_{d0} (1 + l [A])}{X} \quad (18.15)$$

The limit of the expression for K_d at $[A] \rightarrow 0$ is K_{d0} :

$$\lim_{[A] \rightarrow 0} K_d = K_{d0}$$

To exclude X and l we find the first and second derivatives of X and K_d with respect to $[A]$. Combination of the relevant equations yields:

$$K_d'' + \sum_{j=1}^N \beta_j \{K_d [A]^j + 2K_d' [A]^{j-1} + K_d j(j-1) \times [A]^{j-2}\} = 0 \quad (18.16)$$

Designating the expression in braces by a_j , we have

$$K_d'' + \sum_{j=1}^N \alpha_j \beta_j = 0$$

The quantity K_d'' is found by graphical differentiation of K_d as a function of $[A]$ assuming that the equilibrium concentration of the ligand equals the initial one. Taking N values of $[A]$ we can use the obtained system of equations to find all the constants β_j , but only the first of them β_1 is found with sufficient accuracy.

To determine the other constants, Froneus introduces a new function F_1 :

$$F_1 = \left(\frac{1}{K_d} - \frac{1}{K_{d0}} \right) \frac{1}{[A]} \quad (18.17)$$

Combination of the preceding equations yields:

$$F_1 = \frac{1}{K_{d0}} \left[\frac{\sum \beta_j [A]^{j-1} - l}{1 + l[A]} \right] \quad (18.18)$$

It follows from this equation that:

$$\lim_{[A] \rightarrow 0} F_1 = \frac{\beta_1 - l}{K_{d0}} \quad (18.19)$$

The following constants can be found from the equation

$$X_j = (X_{j-1} - \beta_{j-1}) \frac{1}{[A]} \quad (18.20)$$

assuming that $X_0 = X$ and $\beta_0 = 1$.

In this case, we have

$$\overline{X_1} = \frac{X-1}{[A]} = \frac{\sum \beta_j [A]^j}{[A]} = \sum \beta_j [A]^{j-1}$$

etc.

Consequently:

$$\lim_{[A] \rightarrow 0} X_j = \beta_j$$

Froneus also proposed a different method of determination requiring no graphical differentiation. In this case he used the functions f and Φ_1

$$f = \beta_1 \Phi_1 - X_2$$

where

$$X_2 = \frac{X_1 - \beta_1}{[A]}$$

$$\Phi_1 = F_1 K_{d0} = \left(\frac{K_{d0}}{K_d} - 1 \right) \frac{1}{[A]} \quad (18.21)$$

Evidently

$$\lim_{[A] \rightarrow 0} \Phi_1 = \beta_1 - l$$

In the expression for X_2 at low concentrations of the anion $[A]$, we may limit ourselves to the first two terms, whence

$$f = \beta_1 \Phi_1 - \beta_2 - \beta_3 [A]$$

On the other hand, we have

$$f = \frac{(K_{d0}/K_d) \{ (\beta_1 - l) [A] - 1 \} + 1}{[A]^2} \quad (18.22)$$

Next, we plot Φ_1 and f against $[A]$ and, by extrapolating the curves to $[A] = 0$, we obtain Φ_1 and f_0 . Since $f - f_0 = \beta_1 (\Phi_1 - \Phi_{01}) - \beta_3 [A]$, i.e. $\Delta f = \beta_1 \Delta \Phi_1 - \beta_3 [A]$, we obtain:

$$\frac{\Delta f}{[A]} = \beta_1 \frac{\Delta \Phi_1}{[A]} - \beta_3$$

Plotting $\Delta \Phi/[A]$ against $\Delta \Phi_1/[A]$ we find β_1 from the slope of the line, and β_3 from the abscissa intercept. The following constants are determined by drawing up equations $X_j = X_{j-1} - \beta_{j-1}(1/[A])$ and performing graphical extrapolation to $[A] = 0$.

Example of Calculations. To evaluate the stability constants of the complex formed by ions of cerium and lactic acid, the values of K_d have been determined for various concentrations of the anion:

$[A]$, mmol/litre	132	111	101	78.5	67.3	59.0	42.1	33.4	18.0	9.8	0
K_d	7.45	8.93	9.25	14.6	18.8	22.6	37.4	52.6	106.5	210	900

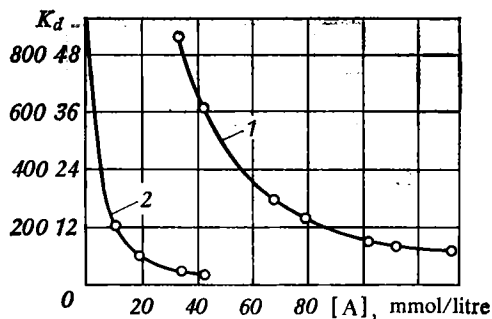


Fig. 18.2. Froneus method. Distribution coefficient K_d against the ligand concentration $[A]$:
 1—for $K_d \times 10^3 < 50$; 2—for $K_d \times 10^3 > 50$

Plot the distribution coefficient K_d against the concentration of the complexing agent $[A]$ (Fig. 18.2).

Calculate Φ_1 by formula (18.21), assuming that $K_{d0} =$

Table 18.1. Quantities Used for Calculating the Formation Constants by the Froneus Method

$[A]$, mmol/litre	K_d	Φ_1	$(\beta_1 - 1) [A]^{-1}$	f	$\frac{\Delta\Phi_1}{[A]} \times 10^3$	$\frac{\Delta f}{[A]} \times 10^4$
0	900	0.257	—	0.058	—	—
10	205	0.339	1.57	0.079	8.2	21
15	137	0.371	2.85	0.088	7.6	20
20	95	0.424	4.14	0.100	8.3	21
25	74	0.446	5.42	0.107	7.6	20
30	60	0.467	6.71	0.113	7.0	18.0
40	39.7	0.542	9.28	0.132	7.0	18.5
50	29.2	0.596	11.85	0.146	6.8	17.6
60	21.9	0.670	14.42	0.165	6.8	18.0
70	17.5	0.720	17.00	0.178	6.6	17.0
80	14.1	0.785	19.56	0.195	6.6	17.0
90	11.1	0.890	22.13	0.222	6.9	18.1
100	9.3	0.960	24.70	0.239	7.0	18.2
110	8.5	0.954	27.27	0.240	6.3	16.5
120	7.8	0.953	29.84	0.238	5.8	15.0

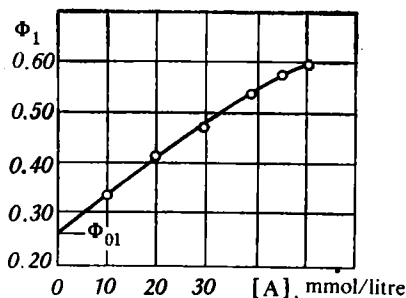


Fig. 18.3. Froneus method. Φ_1 against $[A]$

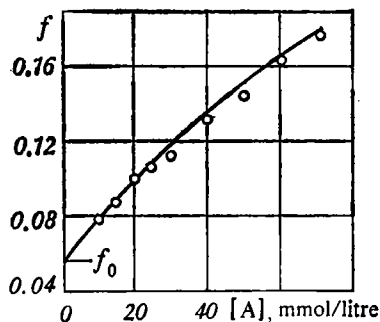


Fig. 18.4. Froneus method. f against $[A]$

= 900 for various values of $[A]$ and of K_d corresponding to them. Tabulate the data (Table 18.1).

Plot Φ_1 against $[A]$ (Fig. 18.3), and, continuing the curve up to $[A] = 0$, find $\Phi_{01} = 0.257$. Find the function f by formula (18.22), assuming that $\beta_1 - l = \Phi_{01}$. Plot f against $[A]$ (Fig. 18.4), and, continuing the curve up to $[A] = 0$, obtain $f_0 = 0.058$ litre²/mmol².

For all the values of $[A]$, find $(\Phi_1 - \Phi_{01})/[A]$ and $(f - f_0)/[A]$, and plot $\Delta f/[A]$ against $\Delta \Phi_1/[A]$ (Fig. 18.5).

From this graph, find

$$\tan \alpha = \beta_1 = \frac{15.84 \times 10^3}{10^4 \times 5.75} = 0.275 \text{ litre/mol}$$

Continuing the straight line up to $[A] = 0$, obtain

$$\begin{aligned} \lim_{[A] \rightarrow 0} (\Delta f/[A]) &= -\beta_2 = 0.8 \times 10^{-4} \text{ litre}^3/\text{mmol}^3 \\ &= 80\,000 \text{ litre}^3/\text{mol}^3 \end{aligned}$$

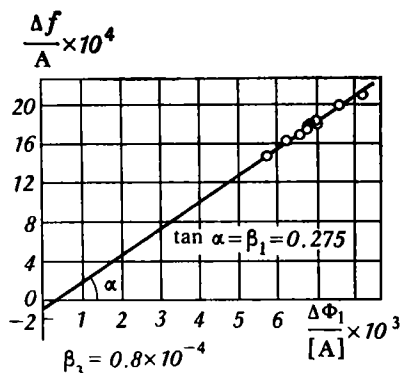


Fig. 18.5. Froneus method. $\Delta f/[A]$ against $\Delta\Phi_1/[A]$

From the equality $\lim f = \beta_1\Phi_{01} - \beta_2$, find $\beta_2 = \beta_1\Phi_{01} - f_0 = 0.275 \times 0.257 - 0.058 = 0.01$ litre²/mmol² = 10 000 litre²/mol². Hence, $\beta_1 = 0.275$ litre/mol, $\beta_2 = 10\,000$ litre²/mol², and $\beta_3 = 80\,000$ litre³/mol³.

C. DETERMINATION OF THE COMPOSITION AND FORMATION CONSTANTS FOR COMPLEX COMPOUNDS OF METALS IN THE +2 OXIDATION STATE BY THE SCHUBERT METHOD

To determine the composition and formation constants of complex compounds in the +2 oxidation state, it is necessary to study the distribution of tracer amounts of their isotopes (⁴⁵Ca, ⁸⁹Sr) between the cation exchanger (KU-2) and a solution of an acid (citric, tartaric, malic). How to prepare the resin in the Na⁺ form is described in Experiment 3.1, Vol. 1.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. A lamp for evaporation. A laboratory shaker. A pH meter. A planchet. Burettes for 25 ml (3). A microburette. A pipette for 10 ml. A micro-pipette for 1 ml. Flasks for 50 ml (7). Test tubes for 10 ml (7) with ground-glass joints.

Radioactive Substances. A solution (10^{-4} M) of SrCl₂ or CaCl₂ containing ⁸⁹Sr (or ⁴⁵Ca) with a specific activity of 100 000 cpm/ml.

Reagents. Resin KU-2 in the Na⁺ form with a grain size of 0.05–0.25 mm (before the experiments, the resin should be saturated with

sodium ions at an ionic strength of 0.16 and a pH of 7.0, after which it should be washed with water and dried at 80°C). Solutions: 0.1 *M* of a complexing agent (citric, tartaric, or malic acid); 0.1 *N* HCl; 0.1 *N* NaOH; 0.5 and 2.0 *M* NaCl.

Performance of Work

Before beginning work, thoroughly wash all the flasks, test tubes, and pipettes that will contain active solutions, rinse them several times with a 0.1 *M* solution of an inactive calcium or strontium salt, and then again thoroughly wash with distilled water.

(a) Determination of Formation Constant for Complex Compound of Sr (Ca) with Citric Acid

Perform all the experiments at a constant ionic strength equal to 0.16 and a pH of 7.0-7.2. At this value of the pH, the concentration of the ligand may be considered numerically equal to that of the citric acid. Prepare solutions with an identical content of $^{89}\text{SrCl}_2$ and an increasing content of the complexing agent. The composition of the solutions is indicated below:

Flask number	1	2	3	4	5	6	7
Volume, ml:							
NaCl, 0.5 <i>M</i>	16.0	16.0	15.9	15.4	14.8	10.0	4.0
Citric acid, 0.1 <i>M</i>	0	0	0.1	0.5	1.0	5.0	10.0
NaOH, 0.1 <i>M</i>	—	—	0.3	1.5	3.0	15.0	30.0
$^{89}\text{SrCl}_2$, 10^{-3} <i>M</i> (or							
$^{45}\text{CaCl}_2$, 10^{-3} <i>M</i>)	1.00	1.00	1.00	1.00	1.00	1.00	1.00

Pour in the volumes of the titrated solutions from the burettes, and the active solutions using a pipette with a syringe or a bulb. After adding the radioactive solution, rinse the flask walls with a small amount of distilled water; neutralize the solution dropwise with an alkali, controlling the pH first with a universal paper indicator, and then with the pH meter. Bring the volumes of the solutions up to 50 ml with water and again stir them.

Transfer 10 ml with a pipette from each flask into one of the marked test tubes containing 50 ml of the resin KU-2. Before doing this, wash the pipette several times with the

solution from the relevant flask. The solution from the first flask (test tube No. 1) is used to determine the value of I_0 and contains no resin.

Put all the test tubes into the shaker and after stirring for two hours transfer them to a stand. After settling of the solutions, take two 1-ml samples from each tube for measuring the β and γ activity using a scintillation detector with a well or after evaporation using a β -counter. Record the results of the measurements, calculate the mean values of the activities, and evaluate the distribution coefficients K_d by formula (3.7) (see Vol. 1), i.e.

$$K_d = \frac{I_0 - I}{I} \frac{V}{m}$$

where I_0 and I are the initial and equilibrium activities of the solution (or its aliquot part), V is the volume of the solution, and m is the mass of the air-dry ion exchanger.

Enter the data obtained into a table.

Data for Determining the Formation Constant:

Entry No.	Concentration of ligand [A]		Distribution coefficient K_d	$\frac{K_{d0}}{K_d}$	$\frac{K_{d0}}{K_d} - 1$	$\log \left(\frac{K_{d0}}{K_d} - 1 \right)$
	mol/litre	log [A]				

Before commencing calculations, plot K_d against [A] and, by extrapolating the curve to a zero concentration of the ligand, obtain the values of $(K_{d0})_{\text{extr}}$. Compare it with the value obtained for the solution containing no citric acid (flask No. 2, test tube No. 2). Use the mean value of K_{d0} for the further calculations. On the basis of the tabulated data, plot $\log [(K_{d0}/K_d) - 1]$ against $\log [A]$ and calculate n and β according to the Schubert method.

(b) Determination of Formation Constant for Complex Compound of Sr (Ca) with Tartaric Acid

The procedure of the experiment is similar to that described in Sec. (a). To provide a constant concentration of the sodium ions and a constant pH of the solutions being studied

(about 7), consecutively add the required solutions to seven 50-ml flasks. The composition of the solution is indicated below:

Flask No.	1	2	3	4	5	6	7
Volume, ml:							
NaCl, 0.5 <i>M</i>	16.0	16.0	15.9	15.7	14.5	13.0	9.0
Tartaric acid, 0.1 <i>M</i>	—	—	0.1	0.5	2.5	5.0	10.0
NaOH, 0.1 <i>M</i>	—	—	0.2	1.0	15.0	25.0	30.0
⁸⁹ SrCl ₂ , 10 ⁻³ <i>M</i> (or							
⁴⁵ CaCl ₂ , 10 ⁻³ <i>M</i>)	1.00	1.00	1.00	1.00	1.00	1.00	1.0

After establishing the required pH (7.0-7.2), bring the volumes of the solutions in the flasks up to the mark. Next proceed as described in Sec. (a).

Use the data obtained to calculate the formation constant of the complex and its composition with the aid of formula (18.12).

*(c) Determination of Formation Constant for
Complex Compound of Sr (Ca) with
Malic Acid*

To provide a constant concentration of the sodium ions at $\mu = 0.16$, pour the following volumes of solutions into seven 50-ml flasks as in the preceding experiment:

Flask No.	1	2	3	4	5	6	7
Volume, ml:							
NaCl, 0.5 <i>M</i>	16.0	16.0	15.9	15.7	14.5	13.0	9.0
Malic acid, 0.1 <i>M</i>	—	—	0.1	0.5	7.5	12.5	15.0
NaOH, 0.1 <i>M</i>	—	—	0.2	1.0	15.0	25.0	30.0
⁸⁹ SrCl ₂ , 10 ⁻³ <i>M</i> (or							
⁴⁵ CaCl ₂ , 10 ⁻³ <i>M</i>)	1.00	1.00	1.00	1.00	1.00	1.00	1.00

After establishing the required pH (7.0-7.2) bring the volumes of the solutions in the flasks up to the mark. Next proceed as described in Sec. (a).

Use the data obtained to calculate the formation constant of the complex and its composition with the aid of formula (18.12).

D. DETERMINATION OF THE FORMATION CONSTANTS FOR COMPLEX COMPOUNDS BY THE FRONEUS METHOD

The Froneus method can be used to determine the composition and stability constant of complex ions of the rare-earth elements with hydroxy acids. The radioactive isotopes ^{141}Ce , ^{147}Pm , and ^{143}Pr can be used for the experiments. It is convenient to use lactic and α -hydroxyisobutyric acids as the ligands. The resin KU-2 in the Na^+ form can be used as an adsorbent. A constant ionic strength of the solutions is provided by adding sodium perchlorate.

The system Ce^{3+} -lactic acid (at $\mu = 0.2$ and a pH of 6.8-7.0) has been taken as an example.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. A lamp for evaporation. A shaker. A pH meter. A burette for 25 ml (3). Flasks for 25 ml (5). A microburette. A pipette for 1 ml. Test tubes for 10 ml with ground-glass joints (9).

Radioactive Substances. A hydrochloric acid solution of $^{141}\text{Ce}^*$ (^{147}Pm , ^{143}Pr) with a volume specific activity of $\sim 50\,000$ cpm/ml.

Reagents. The resin KU-2 in the Na^+ form. Solutions: 20% TBP in benzene, 10 M and 0.4 N nitric acid; 0.4 N H_2A ; 0.2 M NaClO_4 ; 0.2 N NaOH . Lactic acid. α -Hydroxyisobutyric acid.

Performance of Work

Preliminarily calculate the composition of solutions with a ligand concentration of 10^{-4} , 0.001, 0.01, 0.05, 0.10, 0.12, 0.15, and 0.20 mol/litre (respectively) at a constant ionic strength (0.2). Enter the results of calculating the corresponding volumes into a table of the following form:

* If the cerium preparation is contaminated with ^{137}Cs , it is preliminarily purified. For this purpose, the cerium is extracted from 10 M nitric acid with a 20% solution of TBP in benzene and is reextracted with water acidified with HNO_3 . For the cerium to be in the +3 oxidation state, several drops of H_2O_2 are added, the solution is boiled, after which it is evaporated until dry, and the product is washed with a 0.4 N solution of HNO_3 .

Solutions added (for 25 ml), ml			[A ⁻], mol/litre	Calculated value of μ
0.4 N HA	0.2 N NaOH	0.2 N NaClO ₄		

Calculate the concentration of the ligand [A⁻] as the sum of the concentrations of the acid [HA] neutralized by the alkali and the remaining acid dissociating according to the dissociation constant at the given ionic strength:

$$K_{\mu=0.2} = \frac{[H^+][A^-]}{c_{HA} - [A^-]}$$

$$[A^-] = c_{NaOH} + H^+$$

The dissociation constants of lactic (K_1) and α -hydroxyisobutyric (K_2) acids equal 2.35×10^{-4} and 1.80×10^{-4} , respectively.

Put 100 mg of the dry resin KU-2 in the Na⁺ form into each of eight test tubes; keep the ninth tube for controlling adsorption. Pour in 10 ml of the corresponding solution into each tube. Shake the tubes during four hours at a constant temperature. Next take samples of the solutions (1 ml each) for measuring the activity.

Plot K_d against [A]. Compare the value K_{d0} extrapolated to the zero value of the ligand concentration with the experimentally found value. Use the mean value. Draw up tables for the calculations and determine the values of β_1 , β_2 and β_3 . Compare the found values with those contained in the literature.

Repeat the experiments at other values of the ionic strength. Extrapolate the found values of β to an ionic strength equal to zero. Compare the values obtained with published data.

Experiment 18.3. DETERMINATION OF THE SPECIFIC SURFACE AREA BY METHODS OF ISOTOPE AND ISOMORPHIC EXCHANGE [7]

The method of determining the surface area of solid crystalline bodies with the aid of tracer atoms is based on reactions of isotope exchange between the solid substance and its saturated solution containing a radioactive isotope.

In conditions of the absence of recrystallization and extremely slow self-diffusion, isotope exchange is limited only to the surface of the solid. The method gives the value of the true surface area only if the entire surface participates in exchange.

When equilibrium sets in, the radioactive isotope is distributed between the surface of a crystal and the solution in the same ratio as the total number of atoms of the stable isotope distributed on the surface of the crystals forms with the number of atoms in a saturated solution. Taking into account that the measured radioactivity is proportional to the number of atoms of the radioactive isotope, while this number is very small in comparison with the number of atoms of the stable isotope, we obtain

$$\frac{N_{st}}{N_{sln}} = \frac{I_{st}}{I_{eq}} \quad \text{or} \quad N_{st} = N_{sln} \frac{I_0 - I_{eq}}{I_{eq}} \quad (18.23)$$

where N_{st} and N_{sln} are the numbers of atoms of the stable isotope exchanged on the surface and in the solution, respectively, I_{st} is the activity of the solid phase after the establishing of equilibrium, and I_0 and I_{eq} are the initial and equilibrium activities of the saturated solution, respectively.

When an isomorphic labelled compound is used for determining the surface area instead of an isotope one, the quantity D —the crystallization coefficient—must be introduced into the denominators of formulas (18.23). Calculations by the relevant formula give the number of atoms on the surface of a precipitate if the number of atoms in the saturated solution has been found (as is customary practice) according to the solubility of the compound and the volume of the solution.

The relative specific surface area is calculated by the formula

$$\sigma_0 = \frac{LV(I_0 - I_{eq})}{DmI_{eq}} \quad (18.24)$$

where L is the solubility calculated for the cation, g/litre, V is the volume of the solution, litre, and m is the mass of the precipitate, g.

In this case, the relative specific surface area is expressed in grammes of cation per gramme of salt. To go over to the value of the absolute specific surface area σ'_0 expressed in cm^2/g , it is necessary to know the area s falling to each atom

of a molecule being exchanged, which is taken from a reference book or is appraised from the mean distance between neighbouring atoms of the given species by the equation

$$s = \left(\frac{M}{\rho n \times 6.02 \times 10^{23}} \right)^{2/3}$$

where M is the molecular mass of the compound containing n atoms being exchanged, and ρ is the density of the powder.

By multiplying the number of atoms on the surface by the area corresponding to one atom, we obtain:

$$\sigma'_0 = \sigma_0 s n \frac{6.02 \times 10^{23}}{M_M} \quad (18.25)$$

where M_M is the atomic mass of the cation.

The method gives correct results when the magnitude of the surface area does not change during the determination. The conditions of applicability of the method are met the best of all by artificially obtained and thoroughly washed precipitates of sparingly soluble salts in the form of suspensions in their saturated solutions.

The object of the present experiment is the determination of the specific surface area of SrSO_4 by the method of isotope exchange with the use of radioactive ^{89}Sr . Both the surface area of suspensions and that of dry powders are determined.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. A centrifuge and six centrifuge tubes with a capacity of 10 ml provided with ground-glass stoppers. A shaker. A lamp for evaporation. An analytical balance. A small motor with a stirrer. A drying cupboard. A microscope. A planchet. Pipettes for 1 and 5 ml with a syringe. A flask for 50 ml. Glass bowls for measuring activity. Porcelain crucibles (3). A weighing bottle.

Radioactive Substances. A solution of SrCl_2 containing ^{89}Sr with a specific activity of 3.7 MBq/ml (0.1 mCi/ml). A solution of CaCl_2 containing ^{45}Ca with a specific activity of 3.7 MBq/ml (0.1 mCi/ml).

Reagents. 0.1 N SrCl_2 ; 0.1 N MgSO_4 (or a suspension of SrSO_4 in water); a saturated solution of SrSO_4 .

Performance of Work

To determine the surface area of strontium sulphate by the method of isotope exchange, proceed as follows:

(1) prepare finely dispersed solid phases whose surface area does not experience substantial changes in time;

- (2) prepare a saturated solution of the substance to be studied containing a radioactive isotope;
- (3) appraise the duration of establishing of equilibrium between the surface of the substance and the solution;
- (4) find the ratio of the activities of the surface and the solution when equilibrium is reached and calculate the magnitude of the surface area.

*(a) Determination of Surface Area
of SrSO_4 Suspension*

Take a suspension of SrSO_4 prepared by precipitating strontium ions from a dilute solution of SrCl_2 with an equivalent amount of MgSO_4 . Thoroughly wash* the precipitates with water (bidistillate) until a constant value of the electrical conductivity of the washing water is achieved.

Determine the titre of the suspension, i.e. the mass of solid substance in 1 ml of suspension. For this purpose, thoroughly stir the suspension during 30 min with the aid of the mechanical stirrer. Take three samples of 5 ml each with a pipette from the prepared suspension while stirring and transfer them into preliminarily weighed porcelain crucibles. Put the latter into the drying cupboard, evaporate the solution, and dry the residue at 110°C ; find the titre of the suspension according to the mass of the precipitate with account taken of the solubility of the salt.

Prior to the experiment, thoroughly wash all the utensils, but never use sulphuric acid or potassium dichromate when doing this.

Proceeding from the certificate data of the isotope and the conditions of measurement, calculate the volume of the solution that has to be taken for the volume specific activity to be $\sim 10\,000$ cpm/ml.

Put ~ 30 ml of an SrSO_4 solution saturated at room temperature into the 50-ml flask. Pour in the calculated amount of the solution containing ^{89}Sr , but not over 0.5 ml. Bring the volume of the solution in the flask up to the mark with a saturated solution of SrSO_4 .

* A constant value of the surface area is obtained after washing the residues for a long time—about one-and-a-half months. It is recommended to change the water every 3-5 days. The suspensions are prepared beforehand.

Determine the specific activity of the saturated solution. For this purpose rinse the pipette several times and then take two 0.1-ml samples of the solution with it and transfer them into a glass bowl with a filter. Evaporate the solution under the lamp and measure the activity of the obtained samples.

Determine the time needed for equilibrium to set in between the ions of the surface and the saturated solution. Pour 5 ml of the suspension and 5 ml of the active saturated solution of strontium sulphate into each of five centrifuge tubes. Into the sixth tube, which is used to control adsorption, pour 5 ml of an inactive and 5 ml of an active saturated solution of SrSO_4 . Secure the tubes in the shaker and remove them one after another in 1, 5, 10, 20, and 30 min (also remove the control tube in 30 min). Immediately centrifuge the mixtures and take 1-ml samples of the clear solution in glass bowls. Evaporate the solutions and measure the activity of the preparations.

Plot the activity of the saturated solution against the time and determine the time sufficient for achieving equilibrium between the surface and the solution. Use the equilibrium value of the activity to evaluate the specific surface area of strontium sulphate. Take into account that the solubility of strontium sulphate is 1.1×10^{-7} g/litre, the density is 3.96 g/cm^3 , and the area per exchangeable atom is $1.8 \times 10^{-15} \text{ cm}^2$.

(b) Determination of the Surface Area of an SrSO_4 Powder

Filter off about 45 ml of the same strontium sulphate suspension and dry it in the weighing bottle at 110°C up to a constant mass. Keep the powder in the weighing bottle.

Put 50 mg of SrSO_4 into each of four dry test tubes. Keep a fifth tube for controlling the adsorption of the isotope by the tube's walls. Add to each of the tubes 10 ml of the active saturated solution of strontium sulphate with a pipette after first rinsing the latter with the solution. Close the tubes with their ground-glass stoppers and place them in the shaker.

To determine the time needed for the establishing of equilibrium between the surface of the precipitate and the solution, remove the tubes one after another in 5, 10, 20, and

30 min, immediately centrifuge them, and take from each of them two 0.1-ml samples of the clear solution into bowls with a filter on their bottom. Also take two 0.1-ml samples into bowls from the fifth tube after 30 min of mixing. Evaporate the solutions in the bowls under the lamp and measure the activity. Enter the results in a table.

Calculate the relative and absolute specific surface areas of the powder. Compare with the previously determined value for a suspension.

*(c) Determination of Surface Area of SrSO_4
by the Method of Isomorphous Exchange*

Ions of ^{45}Ca are used as the radioactive ion. The value of the crystallization coefficient is preliminarily determined as described in Chap. 2, Vol. 1.

Perform the experiment according to the procedure described above and calculate the value of the relative and absolute surface areas.

*(d) Determination of Surface Area of SrSO_4
Using a Microscope*

For comparison, determine the surface area of strontium sulphate crystals in a suspension. For this end, measure the length, width, and height of the crystals under a microscope, considering them to be right-angle prisms. Calculate the mean value of the surface area for 50-100 measurements. Compare the results obtained by various methods. Use statistical criteria to appraise whether the differences are significant.

**Experiment 18.4. DETERMINATION OF
SATURATED VAPOUR PRESSURE BY THE EFFUSION METHOD
WITH THE USE OF RADIOACTIVE TRACERS [3]**

At present, many methods of measuring saturated vapour pressure are known. Each of them has its inherent optimal limit of pressures being measured that is due to the physical principles of the method, the design of the instrument, and the physicochemical properties of the substance being studied.

The methods in greatest favour for measuring the vapour pressure of poorly volatile substances within the pressure

interval from 10^{-7} to 1 Pa (1 mmHg = 133.322 Pa) are the gas-kinetic methods of M. Knudsen and I. Langmuir.

Knudsen's effusion method is based on measuring the rate at which a vapour flows out from a closed volume through a small calibrated orifice into a vacuum. The pressure of the vapour is calculated by the formula

$$p = G \sqrt{\frac{2\pi RT}{M_m}} \quad (18.26)$$

where p is the saturated vapour pressure, Pa, G is the rate of effusion, $\text{kg}/(\text{m}^2 \cdot \text{s})$, R is the molar gas constant, $\text{J}/(\text{mol} \cdot \text{K})$, T is the temperature, K, and M_m is the mass of one mole, kg/mol .

The rate of effusion is determined according to the mass m of a substance (in kg) flowing out during the time t (in s) through an effusion orifice with a cross-sectional area of σ (in m^2):

$$G = \frac{m}{K\sigma t} \quad (18.27)$$

The Clausing coefficient K has been introduced to take account of the resistance of the effusion orifice to the molecular flux; its value is found from the relevant tables (according to the ratio of the thickness and diameter of the effusion orifice).

The use of radioactive isotopes as labelled atoms makes it possible to considerably simplify the determination of small amounts of an evaporating substance and allows one to determine very small pressures. In this case, the rate of effusion is found from the activity of the condensate:

$$G = \frac{I}{S_0 K \sigma t} \quad (18.28)$$

where I is the activity of the condensate, cps, and S_0 is the specific activity of the initial substance, cps/kg.

Substituting for $2\pi R$ in formula (18.26) its numerical value [$R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$] and using relation (18.28), we obtain

$$p = 7.226 \frac{I}{S_0 K \sigma t} \sqrt{\frac{T}{M_m}} \quad (18.29)$$

If evaporation occurs from an open surface (the Langmuir method), the formula used for calculations is

$$p = 7.226 \frac{I}{S_0 \sigma t \alpha} \sqrt{\frac{T}{M_m}} \quad (18.30)$$

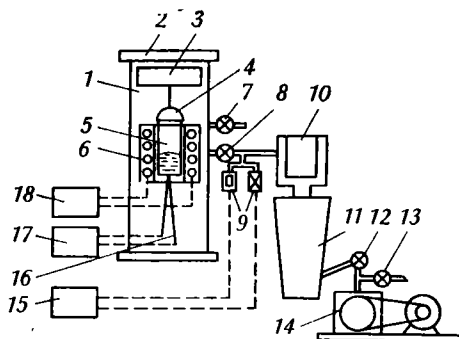


Fig. 18.6.

Schematic diagram of installation for measuring vapour pressure:

1—metal pipe; 2—flange; 3—vacuum manipulator; 4—vapour receiver; 5—effusion chamber with substance being studied; 6—resistance furnace; 7—cock for admitting air into installation; 8—cock; 9—manometric lamps LT-2 and LM-2; 10—cooled trap; 11—high-vacuum pump; 12—cock; 13—cock for admitting air; 14—fore pump; 15—vacuum gauge; 16—thermocouple; 17—device for measuring temperature; 18—heating appliance

where s is the surface area of the evaporating substance, α is what is known as the coefficient of condensation (evaporation)—the fraction of the molecules of the evaporating substance colliding with the surface and condensing on it.

The object of the present experiment is to determine the saturated vapour pressure of zinc. Variants of the experiment include the measurement of the vapour pressure of cadmium, silver, and other elements. The measurements are performed in a special installation consisting of an instrument for determining the vapour pressure, a high-vacuum system, a heating appliance, instruments for control and regulation of the temperature.

Equipment and Reagents

Equipment and Utensils. A counter with a detector provided with a scintillator NaI (TI) having a well. An installation for determining saturated vapour pressure (Fig. 18.6). A microbalance. Measuring flasks for 25 ml (4) and for 1 litre (2). Calibrated flasks for 5-10 ml (5) for measuring the activity. A pipette for 5 ml.

Radioactive Substances. Metallic zinc containing the isotope ^{65}Zn with a specific activity of 370 MBq/g (10 mCi/g).

Reagents. A solution for washing off the condensate: 10 g of inactive zinc in 1000 ml of hydrochloric acid (1 : 1). Nitrogen (liquid).

Instrument for Determining Saturated Vapour Pressure

The designs of instruments for measuring vapour pressure by the effusion method are quite diverse. They may be made from metal and glass and be designed for performing one, several, or a virtually unlimited number of measurements ("single-point", "multiple-point", and continuous-action, respectively) in identical conditions (without disturbing the vacuum and the heating conditions). Depending on whether a molecular beam is used completely or partly for measuring the vapour pressure, integral and differential instruments are distinguished. Provision is often made for connecting a mass spectrometer to the instrument in order to determine the content and molecular mass of the vapour components. In the present experiment, the vapour pressure is measured in a multiple-point instrument of the integral type.

The instrument usually consists of a wide sectional metal (glass) pipe accommodating an effusion chamber heated in some way or other (radiation heating, electron bombardment, induction heating, etc.).

The effusion chamber is a sectional, most often molybdenum block installed on a special support. The block contains a crucible with the substance being studied enclosed by a thin diaphragm with a small calibrated orifice. The material of the crucible and diaphragm is chosen depending on the physicochemical properties of the substance being studied; molybdenum or quartz is used when working with zinc. The temperature of the chamber is determined according to the reading of a thermocouple secured in the body of the chamber. The temperature can also be determined in other ways: using an optical pyrometer, a mercury thermometer, etc.

Figure 18.6 shows a schematic diagram of an installation for determining vapour pressure. Effusion chamber 5 with thermocouple 16 is placed in metal pipe 1 with flanges 2 and is heated by resistance furnace 6. Vacuum manipulator 3 can be used to move the cooled vapour receiver 4—a metal or quartz hollow cap with means for being gripped by the manipulator—up to the effusion chamber. The installation is evacuated by a high-vacuum unit including high-vacuum 11 and fore 14 pumps, cocks 7, 8, 12 and 13, cooled trap 10 and manometric lamps 9 connected to vacuum gauge 15.

Performance of Work

To determine the specific activity of the substance being studied take a weighed sample of several milligrams with an accuracy to 0.0001 g and dissolve it in a small amount of hydrochloric acid. Dilute this solution in a flask up to 1000 ml (exactly), again dilute 10 ml of this solution up to 1000 ml (exactly). Use the latter solution as a standard one. Measure the activity of the solution in special 5- or 10-ml flasks carefully selected as regards their dimensions, and insert them into the well of the scintillator. Measure

the background. Use the data obtained to calculate the specific activity.

Put 0.5-5 g of the substance being studied into the effusion chamber provided with a diaphragm having an orifice measured beforehand. Seal the installation. Close all the cocks. Switch on the fore pump and, after opening cocks 12 and 8, evacuate the installation to a pressure of ~ 1 Pa. Switch on the heating of the high-vacuum pump. In 30-40 min, pour liquid nitrogen into the trap.

After evacuating the installation to the required pressure ($\sim 10^{-3}$ - 10^{-4} Pa), switch on the heating appliance and bring the temperature of the chamber up to the preset value (~ 500 - 700 K). Use the manipulator to lower the receiver close against the chamber into its specially cooled seat, and record the time of beginning of the exposure. Continue the exposure on an average for 10-60 min, keeping the temperature constant. When the required time elapses, lift the receiver, recording the time of termination of the exposure. Set the next value of the temperature and repeat all the operations in the indicated sequence.

Run the experiments at 3-5 values of the temperature. Upon completion of the experiments, switch on the heating of the high-vacuum pump without switching off the fore pump and without stopping the cooling of the high-vacuum pump until its heater cools to a temperature of about 320 K. After cooling of the high-vacuum pump, close cocks 8 and 12, and switch off the fore pump by connecting it by means of cock 13 to the atmosphere. Shut off the water in the cooling system. Use cock 7 to connect the installation to the atmosphere, and unseal the installation. Extract the receiver from it. Wash off the active deposit from the inner space of the receiver with two portions (~ 3 ml) of hydrochloric acid (1 : 1) with an addition of inactive zinc. Next wash the receiver with 3-6 ml of distilled water. Collect the washing solutions in a measuring flask and add water, bringing the volume up to 25 ml.

Take 5 or 10 ml from the solution into a special flask and place it in the scintillator well. Determine the activity of the preparation obtained. Find the amount of condensate in the sample by comparing this activity with that of the standard solution.

Calculate the saturated vapour pressure by formula (18.29). Plot $\log p$ against $1/T$, determine the slope of the straight

line, $\tan \theta$, and calculate the heat of evaporation ΔH_T° (in J/mol) of the substance being studied by the equation

$$\Delta H_T^\circ = R \tan \theta \quad (18.31)$$

where

$$\tan \theta = - \frac{\ln p_2 - \ln p_1}{(1/T_2) - (1/T_1)}$$

or

$$\Delta H_T^\circ = 19.12 \frac{\log p_2 - \log p_1}{(1/T_1) - (1/T_2)} \quad (18.32)$$

Experiment 18.5. DETERMINATION OF DIFFUSIVITY [8]

The diffusion of ions in solutions obeys the Fick equation

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2} \quad (18.33)$$

Substantial difficulties have to be surmounted to determine the diffusivities D of ions, especially at low concentrations. The use of radioactive tracers makes it a quite simple matter to determine the diffusivity of ions. The capillary method of determining the diffusivities is the most convenient one. Its essence consists in the following. A solution of a salt containing a radioactive isotope is placed in a capillary sealed at one end, and the specific activity (in cpm/ml) of the initial solution is determined. The capillary of length l with the solution is placed for a certain time in a large volume of water. The latter is vigorously stirred with a stream of air or a stirrer. During a definite period of time, ions diffuse from the capillary into the aqueous solution. Next the capillary is extracted, and radiometric means are used to determine the total activity and, consequently, the concentration c of the salt remaining in the capillary. If the concentration of the salt at the initial instant c_0 and after the time t is known, then by solving the Fick diffusion equation for the given boundary conditions, we obtain

$$\ln \left(\frac{\pi^2}{8} \cdot \frac{c}{c_0} \right) = - \frac{\pi^2 D t}{4l^2} \quad (18.34)$$

When radioactive tracers are used, the ratio c/c_0 may be replaced by the ratio of the activities I/I_0 of the same volume of the solution before and after diffusion. It must be noted that formula (18.34) holds when $I/I_0 < 0.75$.

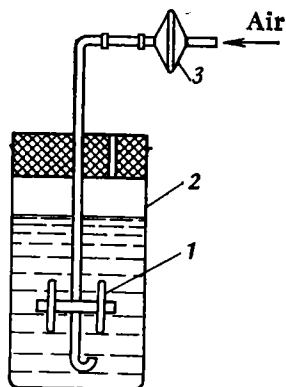


Fig. 18.7. Arrangement for determining diffusivities in solutions: 1—capillaries; 2—beaker with solution; 3—glass filter

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation or a scintillation detector of γ -radiation. A thermostat with an arrangement for determining diffusion (Fig. 18.7). A micrometer or a slide caliper. A set of capillaries with a length of 1.5–2.0 cm and an internal diameter of 0.3–0.5 mm (10). A device for filling and washing capillaries (Fig. 18.8). Glass bowls for measuring the activity.

Radioactive Substances. A solution of NaI (0.1 M) containing ^{131}I with a specific activity of 5×10^5 cpm/ml.

Reagents. A 0.1 M solution of NaI; a 1% solution of Na_2SO_3 .

Performance of Work

Bring the thermostat into its working position; it must maintain a temperature of $25 \pm 0.1^\circ\text{C}$. Assemble an arrangement for determining diffusivities (Fig. 18.7), fill it with water or a 0.1 M solution of NaI and secure it in the thermostat.

Thoroughly (with an accuracy within 0.1–0.05 mm) measure the length of four capillaries. Fill all the capillaries with a 0.1 M solution of NaI containing ^{131}I having a specific activity of 5×10^5 cpm/ml. For this purpose, first wash each capillary by means of a micropipette (Fig. 18.8) with the initial solution, inserting the pipette into the capillary (*handle with care! do not break it!*) and forcing the solution out of it. Next slowly extract the end of the micropipette from the capillary. Use another micropipette to remove the

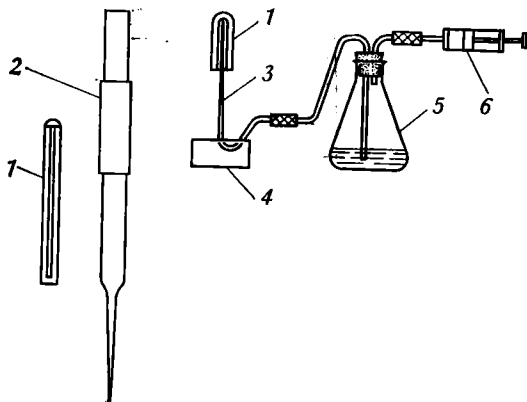


Fig. 18.8. Devices for filling and washing capillaries:
 1—capillary; 2—pipette; 3—capillary tube; 4—glass bowl
 for measuring the activity; 5—conical flask; 6—syringe

solution from the capillary and transfer it into the bottle for radioactive wastes. Repeat this operation twice (*complete saturation of the capillary walls with the initial solution!*). Use the first micropipette to fill all the capillaries with the initial active solution (*no air bubbles should remain in the capillary; the drop of the solution must be at the upper cross section of the capillary!*).

Place the capillaries filled in this way into a holder and put them into the arrangement for measuring diffusivities (it is in the thermostat). Simultaneously start a stop watch. Vigorously stir the solution in the arrangement with compressed air or a stirrer. Continue the experiment at 25 °C during 2-3 h (or at 50-60 °C during 0.5-1 h).

After this time elapses, transfer the content of the capillaries with the aid of the special device (see Fig. 18.8) into the standard glass bowls for measuring the activity with filter paper disks on their bottoms. Extract the solution from the capillaries as follows. Carefully fit each capillary onto thin capillary tube 3 of the device (see Fig. 18.8) and force out the active solution into the bowl with the aid of the syringe or a rubber bulb. Next thoroughly wash the capillary with distilled water and collect the latter in the same bowl.

First acquaint yourself with the operation of the device for washing capillaries.

After transferring the solutions from all the capillaries into the bowls and washing them with distilled water, fill these capillaries with the initial active solution of NaI. In the given case, it is also necessary to preliminarily saturate the walls of the capillaries with the solution. Remove the drop on the capillary with filter paper. Next transfer the content of the capillaries into standard glass bowls with filter paper disks (the device for washing capillaries). Thoroughly wash the capillary with distilled water and put the latter into the relevant glass bowls. Add 3-5 drops of a 1% solution of Na_2SO_3 to each bowl. Evaporate the solutions in the bowls until dry under an infrared lamp. Measure the activity of the preparations obtained with an accuracy up to 2% (*do not confuse the bowls*)*.

Determine I_t/I_0 for each capillary and evaluate the diffusivity. Compare the results of parallel measurements.

Transfer the paper filters from the bowls into a special beaker for dry residues. Thoroughly wash the bowls and micropipettes with distilled water. Pour the washing water into a bottle for radioactive waste.

Experiment 18.6. DETERMINATION OF RATES OF EVAPORATION AND DIFFUSION BY THE METHOD OF ISOTOPE EXCHANGE [2, 3, 9]

Two flat specimens, one of which contains atoms of a radioactive isotope, are placed in a sealed chamber at a certain distance from each other. A rarefaction is created in the chamber. At a sufficiently high temperature, isotope exchange occurs between the specimens. The radioactive isotope is transferred from the "donor" to the "acceptor" by evaporation, while it penetrates into the acceptor by diffusion.

Solution of the relevant diffusion equations yields the mass of the atoms m_2 (in kg) transferred from the donor to the acceptor during the time of exchange t (in s):

$$m_2 = \varepsilon p s t \left(1 - \frac{8\varepsilon}{3} \frac{\sqrt{t}}{\sqrt{\pi} D} + \dots \right) \quad (18.35)$$

* The activity of the capillaries can be measured before and after diffusion in the γ -scintillation counter, using a crystal with a well.

where ρ is the density, kg/m^3 , s is the area of a specimen, m^2 , ε is the linear speed of evaporation, m/s , and D is the diffusivity, m^2/s .

Equation (18.35) contains the quantities ε and D . By studying the kinetics of isotope exchange, one can determine these important characteristics of the evaporation and diffusion processes.

The counting rate for a specimen is proportional to the mass of the atoms of the radioactive element. Therefore, the ratio of the counting rates of the acceptor I_2 and the donor I_1 equals the ratio of m_2 to the mass of the donor m_1 . The average thickness of the donor determined from its mass is

$$h = \frac{m_1}{\rho s} \quad (18.36)$$

The ratio of the counting rates of the acceptor and donor therefore becomes

$$\frac{I_2}{I_1} = \frac{m_2}{m_1} = \frac{\varepsilon t}{h} \left(1 - \frac{8\varepsilon \sqrt{t}}{3 \sqrt{\pi D}} \right) \quad (18.37)$$

For short durations of exchange, we may limit ourselves to the first term of Eq. (18.37):

$$I_2/I_1 = \varepsilon t/h \quad (18.38)$$

Hence

$$\varepsilon = \frac{I_2}{I_1} \frac{h}{t} \quad (18.39)$$

For sufficiently prolonged durations of exchange, but when the deviation from linearity does not exceed 10 per cent, the second term of the series must also be taken into account. This allows one to determine the diffusivity when the speed of evaporation is known. By extrapolating the linear section of the graph of the exchange kinetics to the region of non-linearity, we obtain

$$\left(\frac{I_2}{I_1} \right)_{\text{extr}} = \frac{\varepsilon t}{h} \quad (18.40)$$

Hence

$$\begin{aligned} \Delta &\equiv \left[\left(\frac{I_2}{I_1} \right)_{\text{extr}} - \frac{I_2}{I_1} \right] / \left(\frac{I_2}{I_1} \right)_{\text{extr}} \\ &= \frac{8\varepsilon \sqrt{t}}{3 \sqrt{\pi D}} \end{aligned} \quad (18.41)$$

To evaluate the diffusivity, we obtain the equation

$$D = \frac{64\varepsilon^2 t}{9\pi\Delta^2} \quad (18.42)$$

Equipment and Reagents

Equipment and Utensils. A counter for registering β - and γ -radiation. A vacuum installation with a furnace for heating specimens. Instruments for measuring the vacuum and temperature. A molybdenum container for performing isotope exchange.

Radioactive Substances. Donors—specimens enriched with radioactive ^{110m}Ag (0.01 mCi each) that are silver plates ~ 0.2 mm thick with an area of ~ 0.5 cm².

Reagents. Acceptors—specimens of pure silver having the same dimensions as the donors.

Performance of Work

(a) Determination of Evaporation Speed and Diffusivity

Place the donor and acceptor in recesses in the container and secure the latter with molybdenum wire to the suspension in the vacuum installation. Set the required temperature in the furnace within the interval from 700 to 900 °C. Evacuate the air from the system to $\sim 10^{-2}$ Pa (10^{-4} mmHg) and lower the container into the furnace. Note the time when the experiment is begun. Upon completion of annealing, remove the container from the furnace. After the container cools, remove it from the installation and extract the specimens from the container. Measure the counting rate I_2 of the acceptor and I_1 of the donor.

Determine the thickness of the donor h either directly or from its area s and mass m_1 . Perform the experiments at various exposures and temperatures. For each temperature plot I_2/I_1 against t . Use the slope of the linear portion of the graph to determine the linear speed of evaporation:

$$\varepsilon = h \tan \alpha \quad (18.43)$$

Calculate the mass rate of evaporation [in kg/(m²·s)]:

$$G = \varepsilon \rho \quad (18.44)$$

Evaluate the saturated vapour pressure p (in Pa):

$$p = \frac{228.6G \sqrt{T}}{\sqrt{M_m}} \quad (18.45)$$

where T is the absolute temperature and M_m is the molecular mass of the vapour.

For sufficiently prolonged periods, use the plot of I_2/I_1 against t to determine Δ and calculate the diffusivity by Eq. (18.42).

Compare the results obtained with published data.

(b) Determination of the Heat of Evaporation of a Pure Component

The dependence of the saturated vapour pressure on the temperature is described by the Clausius-Clapeyron equation

$$\frac{d \ln p}{dT} = -\frac{\Delta H}{RT^2} \quad (18.46)$$

If we assume the heat of evaporation to be independent of the temperature, by integrating Eq. (18.46) we obtain

$$p = -\frac{\Delta H}{T} + \text{const} \quad (18.47)$$

The last equation allows one to determine the heat of evaporation according to the known temperature dependence of the saturated vapour pressure.

As described in Sec. (a), determine the vapour pressure of the pure component for several temperatures (4-5 measurements). Use the data to plot $\ln p$ against $1/T$. Determine the slope of the straight line and calculate the heat of evaporation by Eq. (18.47).

Compare the result obtained with published data.

(c) Determination of Activation Energy of a Diffusion Process

The temperature dependence of the diffusivity is described by the equation

$$D = D_0 \exp \left(-\frac{E}{RT} \right) \quad (18.48)$$

where D_0 is a constant, E is the activation energy of diffusion, and R is the molar gas constant.

When the temperature dependence of the diffusivity is known, Eq. (18.48) makes it possible to determine the activation energy of a diffusion process.

As described in Sec. (a), determine the diffusivity for several temperatures (4-5 measurements). Use the data to plot $\ln D$ against $1/T$. Determine the slope of the straight line and evaluate the activation energy of diffusion, using Eq. (18.31) in which

$$\tan \alpha = \frac{\ln D_2 - \ln D_1}{(1/T_1) - (1/T_2)} \quad (18.49)$$

Evaluate E and D_0 by Eq. (18.48) of the temperature dependence of the diffusivity.

Compare the data obtained with published ones.

(d) Determination of the Thermodynamic Activity of a Solid Solution Component

The method of isotope exchange allows one to determine the thermodynamic activity of the components of a solid solution quite readily.

The thermodynamic activity a is determined by the relation

$$a = \varepsilon/\varepsilon_0 \quad (18.50)$$

where ε_0 is the speed of evaporation of a pure component, and ε is the speed of evaporation of the same component from a solution.

Knowing the value of the activity a , we can readily determine the values of the partial molar quantities: the Gibbs free energy ΔG_i , the entropy ΔS_i , and the enthalpy ΔH_i , using well known equations of thermodynamics:

$$\Delta G_i = RT \ln a_i \quad (18.51)$$

$$\Delta H_i = -RT^2 \frac{d \ln a_i}{dT} \quad (18.52)$$

$$\Delta S_i = -R \ln a_i + \frac{\Delta H_i}{T} \quad (18.53)$$

Determine the rate of evaporation of the pure component Ag and of the same component from the solid solution Ag-Sn as described in Sec. (a); perform the measurements at 4-5 different temperatures. Use the equations given above to evaluate the thermodynamic activity a and the partial molar thermodynamic quantities.

Experiment 18.7. DETERMINATION OF SELF-DIFFUSIVITY IN SOLIDS [2, 10, 11]

One way of determining the self-diffusivity is the "thin-layer" method whose essence consists in the following. A very thin layer of a radioactive substance is applied to a thin plate of the material being studied, after which the change in the intensity of irradiation from both sides of the specimen is measured as a function of the holding time in isothermal conditions.

The method can be used in practice only for β - and soft γ -emitters because an appreciable absorption of the radiation in the specimen is needed; the presence of an additional hard γ -radiation does not prevent realization of the method and can be taken into account when measuring and subtracting the background. For a sufficiently long time of isothermal holding and a small thickness of the applied layer in comparison with the thickness of the specimen, the ratio of the radiation flux from the side of the applied layer I_1 to the radiation flux from the opposite side I_2 has the form

$$\frac{I_1}{I_2} = \frac{1 + K \exp(-Bt)}{1 - K \exp(-Bt)} \quad (18.54)$$

where t is the duration of isothermal holding, and K is a constant taking into account the absorption and scattering of the radiation. It follows from the ratio of the fluxes that

$$\ln \frac{I_1 - I_2}{I_1 + I_2} = \ln K - Bt \quad (18.55)$$

where $B = (\pi/l)^2 D$, and l is the thickness of the specimen.

Equipment and Reagents

Equipment and Utensils. A counter for registering β -radiation. A vacuum installation with a furnace for heating the specimens. Instruments for measuring the temperature and controlling the vacuum.

Radioactive Substances. Silver plates ~ 0.1 mm thick with a layer of radioactive ^{110m}Ag applied to them; prior to application of the radioactive layer, the plates should be annealed in a vacuum at $\sim 900^\circ\text{C}$ during 30 min.

Performance of Work

Cut out a specimen with an area of $\sim 0.5\text{ cm}^2$ from a silver plate. Apply radioactive silver to one side of the layer (the total activity of the specimen should be about 500 cps).

It is convenient to do this by electrolysis from a cyanide bath containing a complex salt of radioactive silver.

Determine the intensity of radiation from the radioactive surface of the specimen I_1 . Turn the specimen with its back side to the counter and again measure the intensity of radiation I_2 .

Place the specimen in the furnace. Measure I_1 and I_2 after different periods of isothermal holding.

Use the data obtained to plot $\ln [(I_1 - I_2)/(I_1 + I_2)]$ against t .

Calculate the diffusivity for all the temperatures of the experiment from the relation

$$D = \frac{Bl^2}{\pi^2} \quad (18.56)$$

Perform measurements at different temperatures, and use Eq. (18.48) to determine D_0 and the activation energy E —parameters characterizing diffusion in the given material. Compare the data obtained with published ones.

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Chapter 19 Use of Radioactive Isotopes for Studying the Structure of Chemical Compounds, the Mechanism and Kinetics of Chemical Reactions

Experiment 19.1. STUDYING THE EQUIVALENCE OF ATOMS IN A MOLECULE

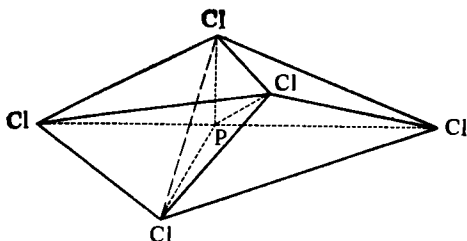
The question of whether the bonds of atoms of the same element in a molecule is equivalent or not is important for understanding the nature and structure of chemical compounds. The answer to it is given by studying the mobility of the atoms in a molecule because it is determined by the nature of the bond of the elements in the given molecule. Information on the mobility of atoms, complex ions, or various parts of a molecule can be obtained by studying the rate of isotope exchange.

It is quite natural that the rates of exchange of equivalent atoms are the same, and of non-equivalent ones are different.

Isotope exchange can be used for studying the structure of a molecule only when it proceeds at a measurable rate, and if the rates of exchange of the non-equivalent atoms differ sufficiently from one another. Owing to the clearly expressed inclination of most inorganic compounds to dissociate (a result of which is very rapid isotope exchange), the investigation of the mobility of the atoms in such molecules by the method of isotope exchange is possible only in complex compounds.

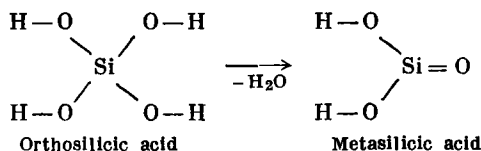
Investigation of the equivalence of the chlorine atoms in phosphorus pentachloride is an example of using the method of isotope exchange. This molecule is usually assumed to have the structure of a trigonal bipyramid with the phos-

phorus atom at its centre:

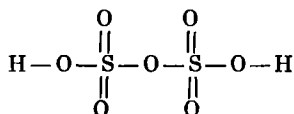


Investigation of the isotope exchange of chlorine ^{36}Cl between PCl_5 and Cl_2 in a solution of CCl_4 showed that three chlorine atoms in the molecule PCl_5 are exchanged rapidly, and the other two are exchanged more slowly. It is evident that the equatorial atoms are exchanged rapidly and the axial ones, slowly.

An interesting case of the equivalence of atoms inexplicable by the structural theory was discovered when studying the isotope exchange in the anions of oxyacids. In the classical form of writing oxyacids, the loss of water by orthoforms corresponds to the appearance in a molecule, in addition to hydroxyl oxygen atoms, of an oxygen atom connected by two bonds to the central atom:



In more complicated cases, it becomes necessary to assume the existence of three types of oxygen atoms, as, for example, in pyrosulphuric acid $\text{H}_2\text{S}_2\text{O}_7$:



Non-equivalence of these atoms that is capable of manifesting itself not only in isotope exchange, but also in conventional chemical reactions, should correspond to the models with two or three structural types of the oxygen atom described above. In this case, the isotope composition of

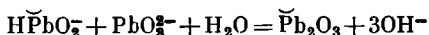
the reaction products should deviate from equal distribution if molecules containing radioactive atoms in a definite position participate in the reaction. Investigation of the isotope exchange of oxygen in acids and salts, however, showed the complete kinetic equivalence of all the oxygen atoms. This signifies that the structural formulas written above do not correspond to actual facts.

In addition to isotope exchange, the equivalence of atoms can also be studied by taking advantage of the ability of atoms to retain their position in a molecule when a series of consecutive chemical reactions are carried out. In this case, a part of radioactive atoms are introduced into the compound being synthesized, and then it is decomposed so that the radioactive atoms are distributed between the products. The non-statistical distribution of the radioactivity indicates the non-equivalence of the atoms within the molecule. Should a statistical distribution of the radioactivity be obtained, the conclusion cannot be made that the atoms are equivalent.

A. STUDYING THE EQUIVALENCE OF THE BONDS OF Pb ATOMS IN A MOLECULE OF Pb_2O_3 [4]

The present experiment is devoted to studying the equivalence of lead atoms in Pb_2O_3 by its synthesis and decomposition.

A labelled compound $\tilde{\text{Pb}}_2\text{O}_3$ is prepared by mixing dilute alkaline solutions of an inactive plumbite and a plumbate labelled with a radioactive lead isotope (ThB). The following reaction occurs:



Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. An analytical balance. A platinum plate. A centrifuge. An emanator for obtaining an active deposit of thoron. Beakers for 100 ml (4). A Büchner filter with a sintered glass filter. Pipettes for 5 and 10 ml with syringes. Planchets for measuring the activity of liquids.

Reagents. $\text{Pb}(\text{CH}_3\text{COO})_2$; $\text{Pb}(\text{NO}_3)_2$. Solutions: 12 *M* and 0.5 *N* KOH; concentrated CH_3COOH ; concentrated HNO_3 ; 0.5 *N* $\text{Ba}(\text{OH})_2$; 0.1 *M* Na_2CO_3 .

Performance of Work

Prepare a solution of K_2PbO_3 . For this purpose, introduce 0.5 g of $Pb(CH_3COO)_2$ into 10 ml of a 12 *M* solution of KOH in small portions (so that the salt will pass completely into the solution). If a slight insoluble brown or pink precipitate (PbO_2) forms, filter the solution. Next neutralize the solution with acetic acid to a pH of 3.

After this, prepare a solution of K_2PbO_2 with labelled lead. For this purpose, dissolve 0.5 g of $Pb(NO_3)_2$ in 10 ml of hot water and mix with an amount of a nitrate solution of ThB (^{212}Pb) such that the activity of 1 ml of the solution will be ~ 3000 cpm. Prepare the nitrate solution by dissolving an active deposit of thoron in nitric acid containing a small amount of $Pb(NO_3)_2$.

Precipitate $Pb(OH)_2$ from the solution by adding 5 ml of a 0.5 *N* solution of KOH. Filter off the precipitate and dissolve it in 7 ml of a hot 12 *M* solution of KOH. Neutralize the $K_2\check{P}bO_2$ solution obtained to a pH of 3. Pour the plumbate and plumbite solutions into a 100-ml beaker, and an orange-yellow precipitate of $\check{P}b_2O_3$ will form. If a precipitate does not appear immediately, gradually add glacial acetic acid to the mixture until a precipitate appears. Place the solution with the precipitate in a centrifuge tube and centrifuge it. Wash the separated precipitate of $\check{P}b_2O_3$ with a 0.5 *N* solution of KOH.

Decompose the precipitate of $\check{P}b_2O_3$ directly in the centrifuge tube with a 12 *M* solution of KOH with heating. Plumbate and plumbite ions form upon its decomposition.

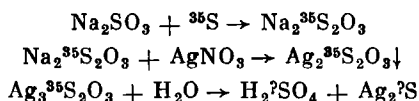
To determine the location (in the plumbite or plumbate) of the radioactive lead, precipitate the plumbate ion in the form of $BaPbO_3$ by adding a surplus of a 0.5 *N* solution of $Ba(OH)_2$. The PbO_2^{2-} remains in the solution. Filter off the precipitate, and wash it several times with a 0.5 *N* solution of KOH. Place the filtrate into a planchet for measuring the activity of liquid preparations. Treat the precipitate of $BaPbO_3$ with a 0.1 *M* solution of Na_2CO_3 with heating. The $BaCO_3$ is less soluble than the $BaPbO_3$, therefore the PbO_3^{2-} ions pass into the solution, while the $BaCO_3$ remains in the precipitate. Filter off the precipitate and place the filtrate into a planchet for measuring the activity of liquids. Measure the activity in both planchets after ra-

radioactive equilibrium sets in between the ThB and ThC (3.5-4 h).

Arrive at conclusions on the equivalence or non-equivalence of the lead atoms in Pb_2O_3 and write its structural formula.

B. STUDYING THE STRUCTURE OF A THIOSULPHATE MOLECULE

Thiosulphuric acid contains two sulphur atoms in its molecule. One of them is assumed to have the -2 oxidation state, and the other $+6$. This, and consequently the structure of a thiosulphate, can be proved by the method of synthesis and decomposition with the use of ^{35}S . The synthesis and decomposition of a thiosulphate can be represented as follows:



In the absence of exchange and with equivalence of the sulphur bonds in a thiosulphate molecule, the radioactive sulphur should be distributed uniformly between the sulphuric acid and the silver sulphate, while if the bonds are not equivalent, it should be concentrated in the Ag_2S .

Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window counter. An analytical balance. A lamp for evaporation. Beakers for 200 ml (2). A measuring glass for 100 ml. A pipette for 1 ml with a syringe. Bowls for measuring the activity.

Radioactive Substances. Sulphur (elementary) containing ^{35}S with a specific activity of $\sim 2 \text{ MBq/g}$ ($50 \text{ } \mu\text{Ci/g}$).

Reagents. Ethanol. Solutions: 0.025 M Na_2CO_3 ; 0.05 M AgNO_3 ; 0.1 M BaCl_2 ; 2 N HCl .

Performance of Work

To obtain a thiosulphate labelled with ^{35}S , dissolve 50 mg of elementary sulphur containing ^{35}S with a specific activity of $\sim 2 \text{ MBq/g}$ ($50 \text{ } \mu\text{Ci/g}$) in 50 ml of a 0.025 M solution of Na_2SO_3 . Add a small surplus of a 0.05 M solution of AgNO_3 to the obtained thiosulphate solution. A precipitate of $\text{Ag}_2\text{S}_2\text{O}_3$ forms, and its hydrolysis leads to the precipitation of Ag_2S and the formation of H_2SO_4 .

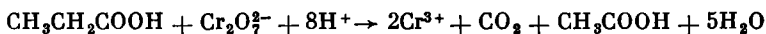
Let the precipitate settle and carefully pour the solution containing the SO_4^{2-} into another beaker. Wash the silver sulphide with water and ethanol by decanting, and transfer it with the pipette into a bowl for measuring the activity. Precipitate the sulphate ion from the solution with a surplus of a 0.2 *M* solution of BaCl_2 in the presence of 5 ml of 2 *N* hydrochloric acid. Decant the mixture after settling, wash the precipitate with water and ethanol by decanting, transfer it with the pipette into another bowl for measuring the activity. Dry the preparations under the lamp for evaporation, and then measure their activity in the counting installation with the end-window counter.

Determine the substance in which the radioactive sulphur is concentrated, and arrive at a conclusion on the structure of a thiosulphate and the equivalence or non-equivalence of the sulphur atoms in it.

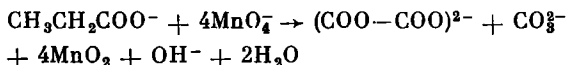
Experiment 19.2. INVESTIGATING THE MECHANISM OF OXIDATION OF PROPIONIC ACID

The method of radioactive tracers makes it possible to establish the mechanism of simple and complicated chemical reactions. It is especially fruitful when studying complicated organic reactions.

The oxidation of propionic acid with potassium bichromate in a strongly acid medium follows the equation



In an alkaline medium, propionic acid is oxidized with potassium permanganate as follows:



In the present experiment, propionic acid labelled with ^{14}C in the carboxyl group is used to study the mechanism of its oxidation by potassium bichromate and permanganate.

Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window counter. An arrangement for oxidizing propionic acid (Fig. 19.1). An apparatus for steam distillation. A sand bath. A centrifuge for 3000 rpm with tubes for 50 ml. A sectional funnel for filtration. A lamp

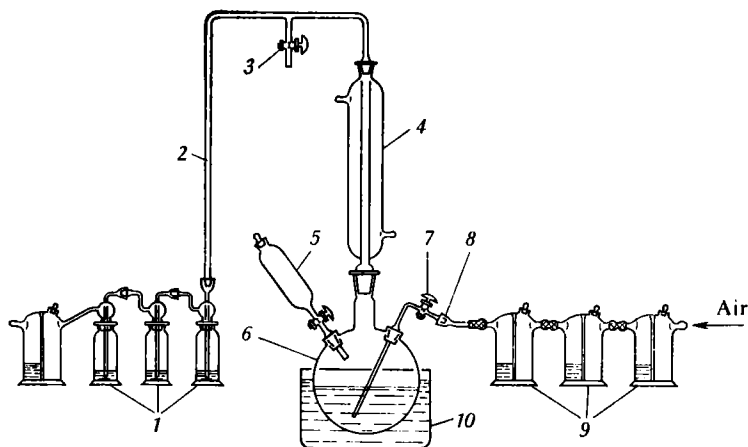


Fig. 19.1. Arrangement for oxidizing propionic acid:
 1—wash bottles; 2—connecting tube; 3—cock; 4—cooler;
 5—dropping funnel; 6—reaction flask; 7—cock; 8—ground-
 glass joint; 9—Tishchenko bottles; 10—water bath

for evaporation. A porcelain bowl. A porcelain mortar. Measuring cylinders for 5-10 ml (2). A pipette for 1 ml with a syringe.

Radioactive Substances. A solution (5 ml, 0.1 M) of propionic ^{14}C acid in 9 M sulphuric acid with a specific activity of ~ 20 kBq/ml ($0.5 \mu\text{Ci/ml}$). A solution (4 ml, 0.1 M) of propionic acid in a 2 N solution of H_2SO_4 (containing no CO_3^{2-} ions) with a specific activity of 10^5 cpm/ml.

Reagents. $\text{K}_2\text{Cr}_2\text{O}_7$; KMnO_4 . Solutions: 0.4 N $\text{Ba}(\text{OH})_2$; 2 N and 30% NaOH ; 1 M CaCl_2 ; 30% H_2O_2 ; 9 M H_2SO_4 .

Performance of Work

(a) Oxidation with Potassium Bichromate in an Acid Medium

Switch on the sand bath. Assemble the apparatus for steam distillation and bring it into a working state.

Assemble the arrangement for oxidizing propionic acid (Fig. 19.1) and connect it to compressed air mains. Pour 50 ml of a 30% solution of NaOH into each of Tishchenko bottles 9, pour 0.50 g of finely triturated $\text{K}_2\text{Cr}_2\text{O}_7$ into three-neck reaction flask 6 and add to it 5 ml of 9 M sulphuric acid.

Fill absorbing wash bottles 1 up to one-fourth of their volume with a 2 N solution of NaOH (without CO_3^{2-} ions).

Introduce 5 ml of a 0.1 *M* solution of labelled propionic acid in 9 *M* sulphuric acid into funnel 5 and close it with its stopper. Admit water into cooler 4.

Close cock 7 and with cock 3 open introduce 5 ml of labelled propionic acid into the reaction flask. Wash the funnel with 15 ml of 9 *M* sulphuric acid. Close cock 3 and heat the contents of the flask during three hours on violently boiling water bath 10. (When adding cold water to the bath, partial sucking of the solution from bottles 1 into connecting tube 2 may occur—this is not dangerous!)

In three hours, without stopping the heating, pass first a weak, and then a strong stream of air for 30 min through the arrangement (cock 3 is closed, and 7 is open!). Absorb the CO_2 evolved as a result of the reaction with a solution of sodium hydroxide.

After scavenging the arrangement with air, disconnect the reaction flask and transfer its contents into the flask of the apparatus for steam distillation. By this instant, the water in the steam generator should violently boil. Distil the formed CH_3COOH with steam until 50 ml of the condensate gathers in the receiver. Add 0.5 ml of a 2 *N* solution of NaOH to the condensate (the reaction of the solution should be alkaline relative to phenolphthalein) and transfer the solution into a porcelain bowl. Evaporate the solution on the sand bath to a volume of 1-2 ml. Transfer the remaining solution into a standard glass bowl with a filter paper disk on its bottom. Evaporate the solution until dry under the lamp for evaporation (*be carefull there must be no splash-ing!*).

Transfer the contents of bottles 1 into a 100-ml beaker and precipitate BaCO_3 by adding to the solution 10 ml of a 0.4 *N* solution of $\text{Ba}(\text{OH})_2$. Filter off the precipitate of BaCO_3 in the sectional funnel through a small-size pore paper filter.

Glue the filter with the slightly moist precipitate to a hard cardboard or aluminium disk and dry it under the lamp for evaporation.

The slightly moist filter can be placed in a special holder and dried in the air. Measure the activity of the obtained preparations.

Use the results of the investigation to arrive at a conclusion on the possible mechanism of the reaction.

*(b) Oxidation with Potassium Permanganate
in an Alkaline Medium*

Assemble an arrangement as shown in Fig. 19.1. Pour 50 ml of a 30% solution of NaOH into each of Tishchenko bottles 9, and pour 0.3 g of finely triturated KMnO_4 into the three-neck reaction flask. Admit water into cooler 4, and pour 5 ml of a 2 *N* solution of NaOH into a separatory funnel. Bottles 1 remain empty. To remove CO_2 , blow air through the arrangement during 10 min (cock 3 is closed, cock 7 is open).

Close cock 7 and via funnel 5 first introduce 5 ml of a 2 *N* solution of NaOH, and then 4 ml of a solution of labelled propionic acid in a 2 *N* solution of NaOH. Wash the funnel with 15 ml of a 2 *N* solution of NaOH.

Heat the reaction flask during two hours on violently boiling water bath 10. Next stop the heating and transfer the content of the flask into a 250-ml beaker. Cool the beaker with the solution with ice and to precipitate MnO_2 carefully (dropwise) add 20 ml of perhydrol (30% H_2O_2). Separate the manganese dioxide by centrifuging or filtration. Transfer the separated clear solution into the reaction flask again, connect it to the arrangement, and blow air through the latter to remove CO_2 . Fill absorbing wash bottles 1 to one-fourth of their volume with a 2 *N* solution of NaOH containing no carbonate ions. While continuing to pass air through the arrangement (cock 3 is closed), add 6-7 ml of concentrated hydrochloric acid to reaction flask 6 from funnel 5. The evolved CO_2 is absorbed during 30 min.

Transfer the contents of bottles 1 into a beaker; precipitate BaCO_3 by adding 10 ml of a 0.4 *N* solution of $\text{Ba}(\text{OH})_2$.

Disconnect the reaction flask and transfer its contents into a 100-ml beaker. By adding a 2 *N* solution of NaOH, produce an alkaline reaction according to methyl red ($\text{pH} \approx 5\text{-}6$), and introduce 10 ml of a 1 *M* solution of CaCl_2 . Cool the contents of the beaker with ice during 30-40 min.

Filter off the precipitates of BaCO_3 and CaC_2O_4 through a small-size pore paper filter in a sectional funnel. Glue the slightly moist precipitates to cardboard or aluminium disks, and only then dry them under the lamp for evaporation. Measure the activity of both preparations.

Use the results to arrive at a conclusion on the mechanism of oxidation of propionic acid by potassium permanganate in an alkaline medium.

Experiment 19.3. INVESTIGATING THE MECHANISM OF OXIDATION OF PHENYLHYDRAZINE [2-7]

The oxidation of phenylhydrazine in aqueous solutions yields benzene. The O—H bonds in the initial molecule or the O—H bonds of the water molecules in whose presence the reaction proceeds may be the source of hydrogen atoms combining with the phenyl radical. This source can be determined by comparing the isotope composition of the benzene obtained upon the reaction of phenylhydrazine with a solution of the oxidizing agent in tritium water and the isotope composition of benzene formed from phenylhydrazine labelled with tritium in the functional group with the conventional aqueous solutions of oxidizing agents (copper sulphate, potassium ferricyanide). Phenylhydrazine labelled in the functional group can be obtained by isotope exchange with tritium water.

The object of the present experiment is the determination of the source of the hydrogen atoms combining with the phenyl radicals when phenylhydrazine is oxidized by aqueous solutions of copper sulphate leading to the formation of benzene. The source of the hydrogen atoms is determined by finding the specific activity of the benzene for various ways of introducing the tritium into the reaction mixture.

Equipment and Reagents

Equipment and Utensils. A counting installation with a liquid scintillation counter. A flask heater. A thermometer for 150 °C. Measuring cylinders for 10 and 50 ml with ground-glass stoppers (2 each). A round-bottom flask for 100 ml. A dephlegmator. A prolong. Separatory funnels for 10 and 50 ml. Receiving flasks (4). A micropipette for 0.1 ml with a syringe.

Radioactive Substances. Water containing ^3H with a specific activity of 37 MBq/g (1 mCi/g).

Reagents. Phenylhydrazine. Sodium (metallic). A 30% solution of CH_3COOH .

Performance of Work

Prepare the following solutions in the 10- and 50-ml cylinders: (1) 40% aqueous CuSO_4 (40 ml); (2) the same in water labelled with tritium having a specific activity of 20-40 MBq/g (1-0.5 mCi/g); (3) 5 g of phenylhydrazine in 5 ml of water

acidified with acetic acid; and (4) the same solution in water labelled with tritium.

Assemble an apparatus for performing the reaction of oxidation of phenylhydrazine and distilling off benzene from the reaction mixture as it is formed (Fig. 19.2). Heat the first solution in flask 1 up to boiling and add solution No. 4 to it dropwise from funnel 2. Distil off the benzene as it forms and gather it in cooled receiver 7. Wash the gathered fraction in the separatory funnel first with water slightly acidified with acetic acid, and then with pure water; dry it with potash, next with metallic sodium, and distil it. Perform experiments in a similar way with solutions 2, 3, and 4.

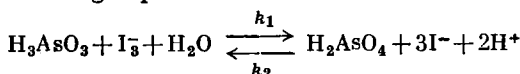
Determine the activity of the obtained benzene. Prepare the counting installation with a liquid scintillation counter. Take samples of 0.05 ml each from the distilled specimens of benzene with the aid of the micropipette and syringe. Transfer the samples into flasks with 5 ml of a scintillation solution [0.5% of 2,5-diphenyloxazol (PPO) + 0.03% 1,4-di(5-phenyl-2-oxazoline)benzene (POPOP)]. Measure the activity of the prepared specimens by the scintillation method. Calculate the specific activity of the benzene with account taken of the effectiveness of the measurements for the isotope ^3H .

Use the data obtained to calculate the degree of transfer of the tritium into the benzene as the ratio of the specific activity of the benzene to that of the initial mixture. On the basis of how the degree of transfer depends on the way of introducing $^3\text{H}_2\text{O}$ into the reaction mixture, arrive at a conclusion as to what hydrogen atoms participate in the formation of benzene in the oxidation of phenylhydrazine.

Experiment 19.4. INVESTIGATING THE KINETICS OF THE REACTION OF OXIDIZING ARSENIC ACID BY IODINE [7]

The method of radioactive tracers makes it possible to determine the rate constant of the direct and reverse reactions in an equilibrium system.

Arsenous acid is oxidized by iodine to arsenic acid according to the following equation:



where k_1 and k_2 are the rate constants of the direct and reverse reactions.

The reaction is reversible. If at the instant when equilibrium sets in, a weightless amount of arsenous acid containing ^{76}As or ^{74}As is added to the reaction mixture, the rate of the appearance of active arsenic(V) v_1 is described by the equation

$$v_1 = \frac{1}{t} \frac{[\text{As}^{3+}] [\text{As}^{5+}]}{[\text{As}^{3+}] + [\text{As}^{5+}]} \ln \left(1 - \frac{I}{I_\infty} \right) \quad (19.1)$$

where $[\text{As}^{3+}]$ and $[\text{As}^{5+}]$ are the total equilibrium concentrations of the arsenic in the +3 and +5 oxidation states, I and I_∞ are the concentration of the arsenic in the +5 oxidation state expressed in terms of the activity of the radioactive arsenic at the instant t and at t_∞ , cpm/ml.

Let $\tau_{1/2}$ be the time during which the reaction proceeds half way, whence $I/I_\infty = 0.5$. Substituting $\tau_{1/2}$ for the time t , we obtain

$$v_1 = \frac{1}{\tau_{1/2}} \frac{0.693 [\text{As}^{3+}] [\text{As}^{5+}]}{[\text{As}^{3+}] + [\text{As}^{5+}]} \quad (19.2)$$

The rate of the reaction of reducing As^{5+} is related to the concentration of the components by the equation

$$v_2 = k_2 [\text{As}^{5+}] [\text{I}^-] [\text{H}^+] \quad (19.3)$$

In equilibrium, we have $v_1 = v_2$ and, consequently,

$$k_2 = \frac{0.693 [\text{As}^{3+}]}{\tau_{1/2} [\text{As}^{3+}] + [\text{As}^{5+}] [\text{H}^+] [\text{I}^-]} \quad (19.4)$$

Equation (19.4) allows us to evaluate the rate constant of the reaction when the system is in thermodynamic equilibrium.

Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window counter. A shaker. An analytical balance. Sectional funnels for filtration (2). A micropipette for 1 ml with a syringe. Test tubes with ground-glass stoppers for 10 ml (3). Beakers for 50 ml (12).

Radioactive Substances. A solution (0.5 M) of Na_2AsO_3 containing ^{76}As with a specific activity of 5×10^4 cpm/ml.

Reagents. A magnesial mixture. KI. Solutions: KBrO_3 (10 g/litre); 0.5 M Na_2AsO_4 ; 1 N HCl; 0.5 M Na_3AsO_4 .

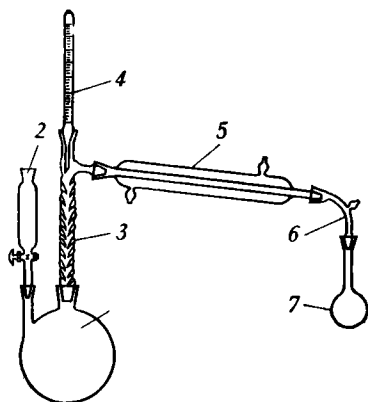


Fig. 19.2. Apparatus for oxidizing phenylhydrazine and distilling benzene:

1—two-neck flask; 2—separatory funnel; 3—dephlegmator; 4—thermometer; 5—cooler; 6—prolong; 7—receiver

Performance of Work

Mix 5 ml of a 0.5 *M* solution of Na_3AsO_4 , 5 ml of a 0.5 *M* solution of Na_3AsO_3 containing ^{76}As , and 5.0 ml of 1 *N* hydrochloric acid in a 25-ml measuring flask and dilute with 10 ml of water, bringing the volume up to the mark. Put 5 ml of the prepared solution in one of the test tubes with a ground-glass stopper. After three or four hours, take two 0.5-ml samples from this tube and precipitate arsenic(V) in the form of $\text{MgNH}_4\text{AsO}_4$. For this purpose, cool two beakers containing 3 ml of distilled water, 5 ml of a magnesian mixture, and 2 ml of concentrated ammonia with ice, and then add to them the 0.5-ml samples. A precipitate forms in 15-20 min. Filter it through paper filters in a funnel for preparing precipitates for measurement of the activity and wash it with a cold dilute ammonia solution. Dry the filters in the air, and then measure their activity.

Arrive at a conclusion on the presence or absence of isotope exchange.

Take two 0.25-ml samples from the measuring flask into two more test tubes and place them into beakers containing a solution of potassium bromate (50 mg of KBrO_3 per 5 ml of water). The potassium bromate completely oxidizes the arsenic(III) to arsenic(V). Next precipitate the arsenate

ion with a magnesia mixture in the cold as described above.

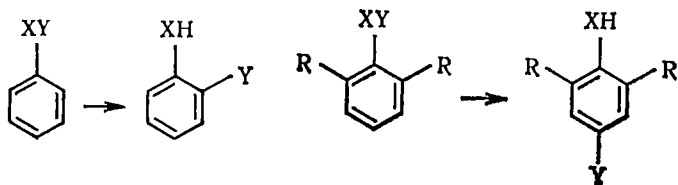
To save time, filter the precipitates simultaneously in two funnels for preparing precipitates for activity measurement. Measure the activity of the obtained specimens. The value of this activity corresponds to that of the AsO_4^{3-} obtained in 0.5 ml of the reaction mixture in equilibrium (I_∞).

Put 0.168 g of solid KI (a sample weighed with an accuracy to within 0.1 mg) into each of two test tubes with ground-glass stoppers, next pour 5 ml of the prepared initial solution from the measuring flask into each tube, place them in the shaker and vigorously stir them. Simultaneously switch on a stop watch. Take 0.5 ml samples from these tubes every 30 min during 2.5-3 h and precipitate the arsenic(V) in the form of $\text{MgNH}_4\text{AsO}_4$ according to the procedure described above. Prepare samples for measuring the activity from the precipitates. Measure the activity (I) of the samples. Plot $\log [1 - (I/I_\infty)]$ against t .

Proceeding from the experimental data, find $\tau_{1/2}$, calculate the rate of oxidation of the arsenic and the rate constant of reduction of the arsenic(V).

Experiment 19.5. INVESTIGATING THE HYDROGEN REGROUPING IN PHENOLS [5, 8]

A large number of regroupings are known in the aromatic series that are of the following type



The method of radioactive tracers makes it possible not only to obtain proofs of the existence or absence of such regroupings, but also to reveal their mechanism.

The object of the experiment is the investigation of the hydrogen regroupings in phenol. Such regroupings may occur either owing to bimolecular processes or as a result of intramolecular reactions. Regroupings occur only through

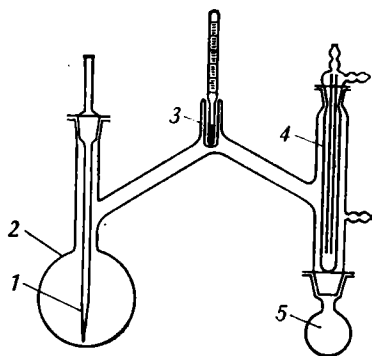


Fig. 19.3.

Apparatus for microdistillation:

1—capillary; 2—flask; 3—holder with thermometer; 4—cooler; 5—receiver

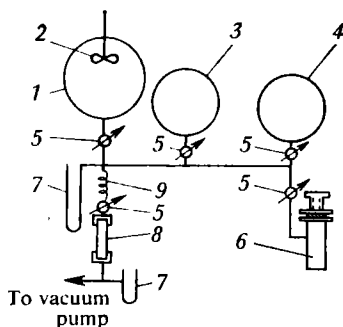


Fig. 19.4.

Arrangement with end-type internal-source counter for determining the activity of organic substances:

1—cylinder for mixing gases; 2—fan; 3—cylinder with helium; 4—reservoir with quenching gas (butane, propane, or cyclohexane); 5—vacuum cocks; 6—device for crushing ampoules; 7—mercury manometers; 8—internal-source counter; 9—capillary

the exchange of the hydrogen in the hydroxyl groups and of the hydrogen in the *ortho* or *para* position in the ring.

The presence of regroupings in alcohols can be proved by measuring the distribution of tritium in a phenol molecule. The molecularity of the reaction can be determined by studying isotope exchange between the molecules of phenol labelled with tritium in hydroxyl and the molecules of the phenol homologue, anisole. The replacement of the hydroxyl group by the methoxyl one does not produce an appreciable change in the chemical properties; such a replacement causes the electron density in the *ortho* and *para* positions to diminish, which may only hamper exchange somewhat.

Equipment and Reagents

Equipment and Utensils. An apparatus for microdistillation (Fig. 19.3). A vacuum arrangement with an end-type internal-source counter (Fig. 19.4), a device for crushing ampoules (Fig. 19.5), and a system for the combustion and absorption of radioactive gases. A horizontal tubular furnace for 700-800 °C. A shaker. A steel container with a screwing on lid. Test tubes with ground-glass stoppers for 25 ml. A micropipette with a syringe for 0.1 ml. A separatory funnel for 50 ml. Coni-

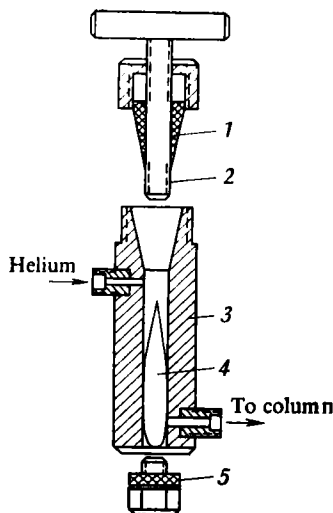


Fig. 19.5. Device for crushing ampoules:
1—fluoroplastic cone; 2—screw; 3 — housing; 4—ampoule;
5—fluoroplastic gasket

cal flasks for 25 ml (4). Ampoules of heat-resistant glass (Pyrex) for 10 ml (3). Ampoules of Superpyrex glass for 100 ml (4). Thin-walled quartz capillaries with a funnel-shaped end (4).

Radioactive Substances. Water containing tritium with a specific activity of 40-200 MBq/g (1-5 mCi/g). An ampoule with gaseous $^3\text{H}_2$ [with an activity of 40 kBq (1 μCi)] and CH_4 (1 : 2).

Reagents. Phenol. Anisole. Diethyl ether. Zinc dust. CaCl_2 . NaCl . NiO .

Performance of Work

(a) Preparation of Phenol Containing Tritium in the Hydroxyl Group

Mix 5 g of phenol with 20 ml of tritium water in a test tube with a ground-glass stopper. Shake the mixture during one hour. Separate the phenol from the water: saturate the aqueous solution with sodium chloride, and then extract the phenol with several 1-ml portions of diethyl ether. After drying the ether solution with calcium chloride and distilling off the ether, distil the phenol in the apparatus for microdistillation (Fig. 19.3).

Seal a weighed sample (5 mg) of the purified phenol in

a quartz capillary for the subsequent determination of the specific activity of the phenol. Put the capillary in a Supercyrex ampoule (100 ml). Weigh 100 mg of nickel oxide and 1 g of zinc dust and also put them in the ampoule with the capillary. Seal the ampoule after evacuating the air to a pressure of 0.1-1 Pa (10^{-2} - 10^{-3} mmHg). By vigorously shaking the sealed ampoule, break the capillary, place the ampoule in the horizontal tubular furnace, heat it to $640 \pm 10^\circ\text{C}$ and hold it at this temperature for one or two hours.

Determine the activity of the mixture of gases formed in the ampoule in an arrangement with an end-type internal-source counter (see Sec. d).

*(b) Investigating the Intermolecular
Isotope Exchange of Hydrogen Between
Phenol and Anisole*

Place 2 g of purified phenol containing tritium in the hydroxyl group together with 2.2 g of anisole into a Pyrex glass 10-ml ampoule. Seal the ampoule after evacuating the air from it (while cooling with liquid nitrogen) to a pressure of 0.1 Pa (10^{-3} mmHg). Put the sealed ampoule in the steel container with the screwing on lid and a heater. Fasten the container with the ampoule in the shaker, heat the cylinder to 200 - 220°C , switch on the shaker, and continue the heating for another 1-3 h.

After cooling the ampoule, open it and transfer its contents into the separatory funnel, washing the ampoule with water and diethyl ether. Saturate the aqueous fraction with sodium chloride, and extract the phenol with several 1-ml portions of ether. Dry the ether solution with a small amount of CaCl_2 . Distil off the ether and then the phenol in an apparatus for microdistillation (see Fig. 19.3). After distillation, the preparation rapidly crystallizes. Also dry the ether fraction with anisole using several grains of granulated CaCl_2 , distil off the ether from it and then the anisole in the apparatus for microdistillation.

Weigh 5 mg of phenol. Use the micropipette with the syringe to take 0.005 ml of anisole. Seal the samples in quartz capillaries (when introducing the samples and sealing the capillaries cool them with liquid nitrogen). Prepare the specimens for burning and burn them as described above. Next measure the activity (see Sec. d).

*(c) Investigating Intramolecular
Isotope Exchange of Hydrogen in Phenol*

Place a weighed portion (2 g) of phenol containing tritium in the hydroxyl group into a Pyrex glass 10-ml ampoule, evacuate the air from it (while freezing the phenol with nitrogen) to a pressure of 0.1 Pa (10^{-3} mmHg) and seal the ampoule. Put the ampoule into the steel container and heat it at 200-220 °C during 1-3 h. After the completion of heating, cool the ampoule and open it. Transfer the phenol into the separatory funnel together with 8 ml of water. Shake the mixture well and then extract the phenol with diethyl ether from a solution saturated with sodium chloride.

After distilling off the ether, repeat the operation of washing the phenol with water. Extract the phenol washed with water and containing no tritium in the hydroxyl group with ether again.

After drying the ether solution of CaCl_2 , distil off the ether and then distil the phenol in the apparatus for microdistillation.

Take 5 mg of the phenol and seal the weighed sample in a quartz capillary. Burn the sample of phenol as described above. Measure the activity of the gas mixture obtained.

Calculate the specific activity of all the samples of phenol and anisole prepared in sections (a), (b), and (c) by the formula

$$S = I \frac{VM}{V_c m}$$

where I is the activity registered by the counter (without the background), cpm, V is the volume of the arrangement filled with active gas, ml, M is the molecular mass of the substance, g, V_c is the volume of the counter, ml, and m is the mass of the substance taken for burning, g.

Calculate (see Vol. 1, Chap. 6) the degree of isotope exchange of hydrogen between water and the hydroxyl group of phenol, between the hydroxyl group and the ring in the phenol molecule, and also between the hydroxyl group of phenol and anisole. By comparing the obtained values, arrive at a conclusion on the mechanism of hydrogen regrouping in phenols.

*(d) Determining the Activity
of Labelled Substances in an End-Type
Internal-Source Counter*

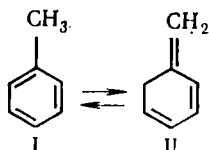
Before beginning work, acquaint yourself with the design and rules for using a vacuum arrangement with an end-type internal-source counter (Fig. 19.4). Prepare the arrangement for work. Place an ampoule with gaseous $^3\text{H}_2$ [with an activity of 37 kBq (1 μCi)] into the device for crushing ampoules (Fig. 19.5) connected to the arrangement for measuring the activity. Seal the arrangement. Evacuate the air from the arrangement first to a pressure of the order of 1 Pa (10^{-2} mmHg) with a fore pump, and then to a pressure of 0.01 Pa (10^{-4} mmHg) with a diffusion pump. After establishing the required rarefaction, disconnect the pumps from the measuring system. By turning the screw in the lid of the device for crushing ampoules (see Fig. 19.5), break the ampoule with tritium. Transfer the active gas into the counter. Note the pressure. Next use the batcher cock to admit butane, or methane, or cyclohexane vapour playing the role of a quenching addition into the system to a pressure of 5×10^3 Pa (40 mmHg). After this pressure is reached in the system, close the batcher cock. By measuring the activity of the gas mixture, find the plateau of the end-type counter. After measuring the activity of the standard specimen with gaseous tritium, again evacuate the system to 0.01-0.1 Pa (10^{-4} - 10^{-3} mmHg). Next open the device for crushing ampoules and remove the ampoule fragments from it. Load the device with an ampoule containing a mixture of H_2 and CH_4 in a ratio of 1 : 2 up to 266 Pa (2 mmHg). Perform all the operations described above with this sample and determine the background of the counter. Similarly, loading the arrangement with ampoules containing burnt samples of phenol or anisole, measure their activity.

Discharge the tritium from the arrangement into the ventilation system or burn it to water and collect it.

**Experiment 19.6. INVESTIGATING THE
TAUTOMERIC TRANSFORMATIONS OF TOLUENE**

In discussions of the mechanism of the toluene halogenation reaction, the assumption of tautomeric transformations

was advanced:



According to quantum-mechanical appraisals, the tautomer II is not advantageous from an energy viewpoint and should not form in noticeable amounts. It was assumed that in conventional conditions equilibrium is shifted in the direction of formation of tautomer I, but in more rigorous conditions, for example upon heating, irradiation with ultraviolet light, with radiation action, etc., formation of tautomer II is possible.

The object of the present experiment is to study the possibility of tautomerization of toluene when heated by studying the change in the intramolecular distribution of tritium atoms in labelled toluene originally containing tritium in the methyl group. Such a change could be a proof of tautomerization.

Equipment and Reagents

Equipment and Utensils. A counting installation with a liquid scintillation counter. A drying cupboard. A three-neck flask with a reflux condenser and a stirrer. A Büchner filter. A funnel for hot filtration. An ampoule of heat-resistant glass (Pyrex) for 5 ml. A pipette for 1 ml with a syringe. A microsyringe.

Radioactive Substances. Toluene containing tritium in the methyl group, with a specific activity of 40 MBq (1 mCi/g).

Reagents. KMnO_4 . HCl (density 1.19 g/cm³).

Performance of Work

Use the pipette with a syringe to take 1 ml of toluene labelled with tritium in the methyl group and transfer it into an ampoule of Pyrex glass (5 ml). Seal the ampoule and heat it in the drying cupboard at 170 °C for at least three hours. After cooling the ampoule, open it and transfer the toluene into the three-neck flask provided with a reflux condenser and a stirrer. Add 70 ml of water to the flask and heat the mixture up to boiling. While vigorously stirring, gradually introduce 3.5 g of well triturated KMnO_4 .

Boil the mixture up to complete decolorization. Filter the hot solution, and wash the precipitate on the filter with hot water. Acidify the filtrate containing potassium benzoate with hydrochloric acid and cool it. Separate the precipitated benzoic acid crystals on the filter, wash them with a few drops of acidified water, and dry at 80-90 °C in the drying cupboard (in Petri dishes).

Determine the specific activities of the initial toluene and the obtained benzoic acid. Before commencing measurements, acquaint yourself with the design and rules for work with an installation having a liquid scintillation counter. Measure the background. Prepare samples for counting: take a weighed portion (5-10 mg) of benzoic acid; use the microsyringe to take 0.01 ml of toluene labelled with tritium, and dilute the sample with 1 ml of inactive toluene. Again take 0.01 ml from the diluted sample. Introduce the samples into bottles with the scintillation solution and measure their activity. Calculate the specific activities of the preparations with a view to the effectiveness of counting for the isotope ^3H .

Find the fraction of the activity in the methyl group and in the ring of toluene subjected to heating. Arrive at conclusions on the possibility of tautomeric transformations of toluene.

Experiment 19.7. DETERMINATION OF THE ISOTOPE EFFECT IN DEHYDRATION OF FORMIC- ^{14}C ACID

Dehydration of formic acid is a first-order reaction. The isotope effect in the decomposition of HCOOH can be appraised from the kinetics of the decomposition process:

$$\Delta = \frac{k_{12} - k_{14}}{k_{12}} \times 100\%$$

where k_{12} is the rate constant of the reaction of dehydration of H^{12}COOH , and k_{14} is the same for H^{14}COOH .

Equipment and Reagents

Equipment. An arrangement for the dehydration of formic acid (Fig. 19.6).

Radioactive Substances. Labelled formic acid (an azeotropic mixture with water) containing ^{14}C with a specific activity of 200 MBq/g (6 $\mu\text{Ci/g}$).

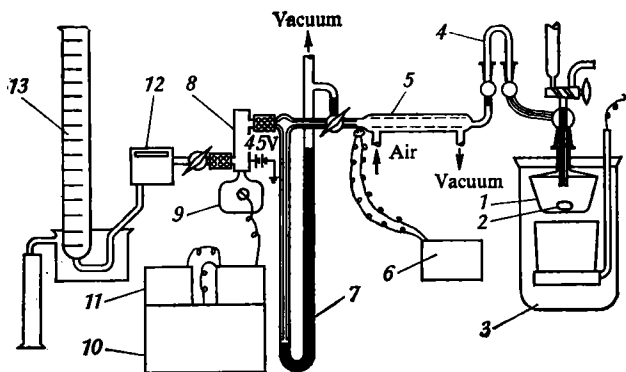


Fig. 19.6. Arrangement for determining the isotope effect in the dehydration of formic acid:

1—reaction flask; 2—magnetic stirrer; 3—thermostat; 4—trap and drier; 5—heat exchanger; 6—thermoregulator; 7—mercury manometer; 8—flow-type ionization chamber; 9—vibration electrometer; 10—recorder; 11—potentiometer; 12—voltmeter; 13—receiver with dibutylphthalate

Reagents. H_2SO_4 (chemically pure) degassed with shaking during 20 h at room temperature and a pressure below 133 Pa (1 mmHg). Ascarite. Drierite. Dibutylphthalate.

Performance of Work

Perform the dehydration of formic acid in the arrangement shown in Fig. 19.6.

Introduce 127 ml of sulphuric acid into Pyrex glass flask 1 placed in thermostat 3 and while vigorously stirring add a solution of 2.36 g of labelled formic acid and 11 ml of preliminarily cooled sulphuric acid to prevent the temperature of the reaction mixture from rising above that of the thermostat. Pass the evolved CO through trap 4 with a mixture of ascarite and drierite and further through copper heat exchanger 5 for establishing thermal equilibrium with the surroundings. Control the pressure of the gas with the aid of mercury manometer 7.

As soon as the CO gets into stainless steel ionization chamber 8, begin to register the activity. Measure the ionization current corresponding to the specific activity and due to the isotope effect according to the voltage drop across a high-ohmic resistor with a known resistance ($10^{12} \Omega$) and use the recorder to register the voltage (in mV) against the time

(in min) in the form of a smooth curve. For each point of this curve, take the corresponding reading of the voltage and add to it the relevant reading of the potentiometer compensating the major part of the voltage in the electric circuit. This yields the values of the specific volume activity during the time t expressed in millivolts. Next reduce these values to standard conditions using a correction taking into account the volume of the gas in the chamber (in moles) and the effectiveness of operation of the chamber depending on the pressure. Use the values of the activity including this correction to plot the activity against the time.

Determine the value of the rate constant of decomposition of the inactive formic acid simultaneously by measuring the total volume of the gas evolved with time. Determine the difference between the rate constants of the reactions ($k_{12} - k_{14}$) graphically according to the slope of the straight lines obtained in the coordinates of the logarithm of the specific activity against the time. Calculate the magnitude of the isotope effect (in %).

Determine the isotope effect at a fixed temperature within the interval from 0 to 25 °C.

Experiment 19.8. USE OF THE EMANATION

METHOD FOR INVESTIGATING SOLID-PHASE TRANSFORMATIONS [1]

The emanation method is one of the methods used to study the physicochemical properties of solids with the aid of radioactive isotopes. It is based on studying the diffusion of radioactive inert gases from solid bodies containing isotopes of radium or thorium. Emanation is characterized quantitatively by the emanation coefficient E . It is determined by the probability of atoms of the inert gas escaping from the solid.

The emanation coefficient consists of two terms, the first of which E_r is due to the effect of radioactive recoil, and the second E_d to the diffusion of radon in the solid:

$$E = E_r + E_d \quad (19.5)$$

In the simplest case, when the atoms of the parent isotope are uniformly distributed over a spherical particle of ra-

dus r :

$$E_r = \frac{3}{4} \frac{R_r}{r} - \frac{1}{16} \left(\frac{R_r}{r} \right)^3 \quad (19.6)$$

$$E_d = \frac{3}{r} \sqrt{\frac{\bar{D}}{\lambda}} \quad (19.7)$$

or, with account taken of the relation

$$D = D_0 \exp(-Q/RT) \quad (19.8)$$

$$E_d = \frac{3}{r} \sqrt{\frac{\bar{D}}{\lambda}} \exp(-Q/2RT) \quad (19.9)$$

where R_r is the path of a recoil atom (Rn) in the solid, r is the radius of a particle, D is the diffusivity of radon, λ is the decay constant of radon, D_0 is a preexponential factor, R is the molar gas constant, Q is the activation energy of radon diffusion, and T is the absolute temperature.

The emanation coefficient E_r does not virtually depend on the temperature; the dependence of E_d on the temperature is described by Eq. (19.9). At room temperature, the contribution of E_d is negligibly small, hence $E = E_r$. This allows one to determine the value of r from Eq. (19.6). The contribution of E_d at higher temperatures is determined according to the difference

$$E_d = E - E_r$$

The presence of phase transformations leads to deviation of the shape of the temperature dependence of E_d (or I) from normal, which makes possible the conclusion on the presence of some process or other in the solid within the given temperature region. The nature of the transformation is determined by comparison with the results of other methods of physicochemical analysis. This is why a combined emanation and thermal analysis is performed that makes it possible to register curves of differential thermal analysis (DTA), thermogravimetric analysis (TGA), and dilatometric analysis (DDA) in identical conditions.

The merits of the emanation method include its high sensitivity, the possibility of studying processes that are not registered by other methods, and its comparative simplicity of embodiment. To perform emanation and thermal analysis, it is necessary to introduce into the substance being studied radioactive isotopes that produce emanation

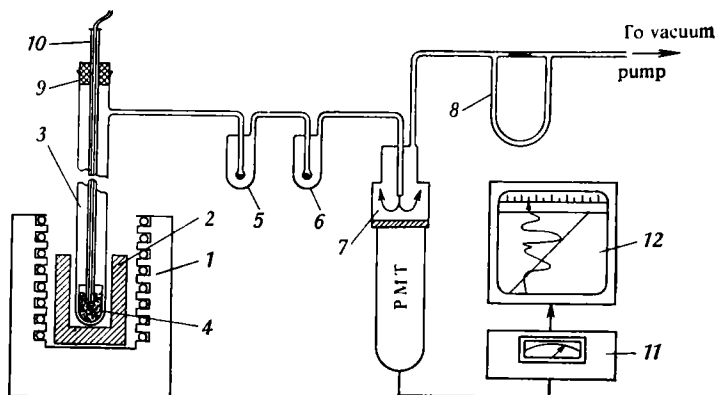


Fig. 19.7. Arrangement for studying emanation:
 1—furnace; 2—steel block; 3—quartz tube; 4—quartz beaker; 5—wash bottle with sulphuric acid; 6—trap; 7—scintillation chamber; 8—rheometer; 9—stopper; 10—thermocouple; 11—integrator; 12—recording potentiometer

atoms upon their transformation, and to observe the rate of evolution of the emanation upon a uniform elevation of the temperature with the aid of a detector of radioactive radiation.

When isotopes of the thorium series are used: $^{228}\text{Th} \xrightarrow{\alpha} ^{224}\text{Ra} \xrightarrow{\alpha} ^{220}\text{Rn} \xrightarrow{\alpha}$, the degree of emanation of a substance can be continuously measured, and hence its changes in the process of heating can be observed.

In the present experiment, the emanation method is used for: (1) detecting the polymorphic transformation of aragonite into calcite, which cannot always be done with the aid of thermographic methods; (2) determining the emanation coefficients and calculating the diffusion parameters of radon in calcium oxide; (3) analysing salts of thorium (^{232}Th), for which purpose it is sufficient to use thorium compounds in equilibrium relative to radiothorium (^{228}Th).

Perform the experiment in the arrangement shown schematically in Fig. 19.7. The arrangement includes a furnace and a device for measuring the activity of the gas. Crucible furnace 1 contains steel block 2 ensuring uniform heating. Quartz tube 3 with quartz beaker 4 half filled with the substance being studied containing radiothorium is lowered

into block 2. The tube is secured in the furnace with the aid of an asbestos-cement plug. A side arm of the tube is connected to wash bottle 5 filled with concentrated sulphuric acid and followed by trap 6 connected to scintillation measuring chamber 7 (the volume of the chamber is 600 ml, and its internal walls are coated with a phosphor based on ZnS). The outlet opening of the chamber is connected via rheometer 8 to a vacuum pump that discharges the gas into a special draught offtake.

The activity of the gases is registered in an installation with a scintillation detector of α -radiation of gases. The counts from the photomultiplier tube (PMT) are fed to integrator (ISS-3) 11 connected to multiple-point recording potentiometer 12.

Equipment and Reagents

Equipment and Utensils. An installation for registering the radioactivity of gases with a scintillation detector of α -radiation. An arrangement for studying emanation. A platinum-platinum + rhodium thermocouple. Quartz beakers for specimens with a capacity of 0.5 ml. A pipette for 0.1 ml. Beakers for 20 ml (4). A beaker for 200 ml. Funnels (2). A desiccator. A Dewar flask.

Radioactive Substances. A hydrochloric acid solution containing ^{28}Th — ^{224}Ra with a specific activity of 50 000 cpm/ml. A standard solution in 5% hydrochloric acid containing ~ 5 mg of ^{232}Th in equilibrium with the decay products. A standard preparation: barium palmitate with a known specific activity of $S_{\text{st}} \approx 400$ Bq/g (10^{-8} Ci/g) and $E_{\text{st}} = 0.9$.

Reagents. $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (pure for analysis). $(\text{NH}_4)_2\text{CO}_3$. A sulphuric acid solution of diphenylamine. $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$. $\text{Th}(\text{SO}_4)_2 \times 9\text{H}_2\text{O}$. $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$. $\gamma\text{-Al}_2\text{O}_3$ (roasted).

Performance of Work

(a) Preparation of CaCO_3 in the Form of Aragonite

Depending on the conditions of precipitation of CaCO_3 , it can be prepared in various modifications—aragonite and calcite.

Perform all the operations in a cupboard for work with α -radioactive isotopes or in a plastic glove box.

Place a weighed portion (2 g) of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in a small beaker and dissolve it in 5 ml of distilled water. Prepare a solution of 0.9 g of $(\text{NH}_4)_2\text{CO}_3$ in 5 ml of cold

distilled water in another beaker. Transfer a drop of the first solution into the second one with the pipette and vice versa. Filter the turbid solutions. Add 0.5 ml of a solution containing radiothorium ($\sim 25\,000$ cpm) to the filtrate of the calcium nitrate solution. (The presence in the solution of small amounts of strontium salts facilitates the formation of aragonite.) Pour both filtrates simultaneously dropwise and with stirring into a beaker with 20 ml of boiling water and boil it another 2-3 min. Let the precipitate settle, check the completeness of precipitation, and if necessary add a little $(\text{NH}_4)_2\text{CO}_3$. Filter off the CaCO_3 in a funnel with suction and wash it with about 150 ml of water up to complete removal of the NO_3^- ions (test with diphenylamine). Dry the washed precipitate at 110°C .

(b) Preparation of CaCO_3 in the Form of Calcite

Proceed in the same way as described in Sec. (a), but pour the solutions of $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{CO}_3$ into cold water.

Place the preparations into small quartz beakers and store them in weighing bottles placed in the desiccator.

(c) Emanation and Thermal Analysis of CaCO_3

Place a weighed portion (~ 200 mg) of the substance being studied in a small beaker and lower it onto the bottom of a tube secured in a metal block. Put the junction of a simple thermocouple in the specimen, and of a differential one into the standard specimen ($\gamma\text{-Al}_2\text{O}_3$) placed in a similar beaker. Immerse the cold junctions into the Dewar flask filled with ice and water.

Switch on consecutively all the elements of the counting installation (the high-voltage voltage stabilizer, the counting device, the integrator ISS-3, the electronic potentiometer). Let the installation warm up for 10-15 min. Switch on the "Check" tumbler switch and register the readings of the instrument on the tape of the potentiometer. Switch on the "Operation" tumbler switch and supply a voltage from the high-voltage stabilizer at which the counting rate of the background is 2-3 cpm.

Connect the standard specimen containing about 5 mg of ^{232}Th in equilibrium with its decomposition products to the chamber via a three-way cock. Set a rate of flow of the air

stream at which the maximum activity of the thoron is registered (see Experiment 13.4). Again register the background of the instrument.

Connect the specimen being studied to the measuring chamber via a three-way cock after choosing the corresponding counting range on the integrator.

Switch on the furnace and set a heating rate of 5-7 K/min with the aid of its autotransformer. After recording the heating curves up to 1000 °C, switch off the furnace and record the cooling curve to room temperature at the same rate of temperature change.

After cooling the furnace, suck air through the emanation chamber, having first switched off the specimen, until a value of the activity close to that of the background sets in.

Switch off all the elements in the reverse sequence to switching on, fasten the thermocouples in a special holder, transfer the specimen being studied into a weighing bottle and hand it in to the laboratory assistant.

Using a calibration curve* for measuring the temperature of the thermocouple, plot curves of the emanation activity against the temperature and the logarithm of the activity against $1/T$.

Repeat the experiment with an aragonite specimen. Compare the curves obtained for aragonite and calcite. Find the temperature of polymorphic transformation of aragonite into calcite and the temperature of decomposition of CaCO_3 .

* Should no thermocouple calibration chart be available, check the correctness of the readings on the potentiometer scale according to reference points.

For temperature calibration of the potentiometer, take substances as specimens whose phase transition temperatures are known beforehand. It is good to use KNO_3 with phase transition temperatures of + 127.8 °C and + 336 °C and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ with a phase transition temperature of + 32.4 °C.

After recording the curves, establish the phase transition temperatures. For this purpose, draw horizontal straight lines from the peaks on the differential curve up to their intersection with the curve of temperature recording. The points of intersection are the phase transition temperatures. After calculating how many millimetres on the tape correspond to one kelvin, graduate the potentiometer scale. Construct a temperature straightedge by means of which the scale graduations can be converted into kelvins.

*(d) Determining the Parameters of
Radon Diffusion in Calcium Oxide*

The experimental data obtained when registering the activity of radon in the cooling process or upon the repeated heating of the residue remaining after the decomposition of the calcium carbonate can be used in the experiment. Enter the data in a table. Plot curves of I against T .

For the initial section, determine the values of I corresponding to the recoil effect and by Eq. (19.6) evaluate the mean size r of the spherical particles. Assume that the path of the recoil atoms in CaO is $R_r = 30$ nm. Calculate E_d and D .

The stages of the calculations require a knowledge of the coefficients making it possible to evaluate the emanation coefficients E_i at the relevant temperatures.

For this purpose, use a standard substance with a known emanation coefficient. Most often barium palmitate (or stearate) containing ^{228}Th is used. For the standard specimen (we shall consider it to be radium-barium palmitate), its specific activity S_p and emanation coefficient E_p are known.

Measure the activity I_p of the radon evolved from the palmitate by placing a weighed sample of mass m_p into a beaker similar to the one containing the sample being studied, completely retaining the other conditions of measurement.

To determine the specific activity of the preparation being studied, weigh the beaker with CaO extracted from the installation, transfer it into a small quartz beaker, add 10 ml of HCl (1 : 1) and, covering it with a watch glass, heat it a few minutes.

Transfer the solution into a bubbler and rinse the beaker with 1 % HCl. Equalize the level of the liquid in the bubbler with that of the standard solution having a known activity A_{st} of the $^{228}\text{ThCl}_4$. Measure the registered activity I_{st} of the standard and I_x of the dissolved CaO. Calculate the mass m_x as the difference between the mass of the beaker with the sample and without it. Calculate the absolute A_x and specific S_x activity of the substance being studied using the expressions

$$A_x = \frac{I_x}{I_{st}} A_{st} \quad \text{and} \quad S_x = \frac{A_x}{m_x}$$

Evaluate the emanation coefficient E_x of the CaO being studied for the given temperature:

$$E_x = E_p K \frac{I_{xmp} S_p}{m_x I_p S_x} \quad (19.10)$$

The quantity K is a constant one for given conditions that allows one to convert the values of the registered activity of the gas I_{xg} to the values of the emanation coefficients corresponding to them. Introduce the values of E_x into a table and fill in the other columns of the table, assuming that the dimensions of the particles and, consequently, of E_r do not change up to 1000 °C.

Entry No.	$t, ^\circ\text{C}$	T, K	I_{xg}	E	$E_d = E - E_r$	D	$\log D$	$1/T$

Use the obtained data to plot D against $1/T$, calculate D_0 and Q , and compile an equation of the dependence of D on T . Appraise the errors in determining D_0 and Q .

(e) *Emanation and Thermal Analysis of Thorium Salts*

Place a weighed portion (~200 mg) of a thorium salt in a quartz beaker and secure it in the quartz tube of the arrangement described above. Perform the analysis with heating up to 1100 °C; obtain curves of cooling and repeated heating of the preparations. Plot emanograms in the coordinates I against t and $\log D$ against $1/T$. Explain the nature of each of the registered effects. Compare the curves obtained with those described in the literature.

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TO THE READER

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